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RESEARCH & DEVELOPMENT OF A HIGH CAPACITY NONAQUEOUS SECONDARY BATTERY

SECOND QUARTERLY REPORT

Contract No. NAS 3-6017

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA

Lewis Research Center

Space Power System Division

21000 Brookpark Road

Cleveland, Ohio

P. R. Mallory & Co. Inc.
Laboratory for Physical Science
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I. THE LITHIUM ELECTRODE

A. Introduction

In this section we shall discuss the manner in which the electrochemical behavior of the lithium electrode may serve as a useful tool in a preliminary assessment of electrolyte purity.

B. Electrochemical Characterization of the Lithium Electrode.

1. Anodic E vs. i measurements (Polarization curves).

a. Experimental. Such measurements are made under steady state conditions in which a long or short pulse of constant current is applied to the working electrode and the resultant potential measured.

b. Results. Anodic E vs. i curves have been reported by others in graphical and tabular form for bulk lithium metal and for other active metals. In the absence of appropriate corrections for iR drop it must be assumed that such data normally reflects the particular cell geometry employed. Though such measurements are useful in the investigation of electrodes to be employed in highly conductive aqueous media they are of questionable significance in the type of systems currently under study.

2. Anodic E vs. t measurements (Chronopotentiograms, Discharge curves)

a. Experimental. Such measurements are made by applying constant current to the working electrode and measuring the resultant potential variation with time.

b. We have repeatedly used such measurements in the past for determining the anodic utilization of electrodeposited lithium. Typically, such measurements have been made at currents of the order of 5 mA cm^{-2} for deposits of the order of 1000 mC cm^{-2} . During this quarter measurements have been made for larger currents and larger amount of deposit. For comparison it will be recalled that the capacity of alkaline secondary cell

electrodes is about 30,000 to 300,000 mC cm⁻².

In Figure 1 are shown two anodic discharge curves for electrodeposited lithium metal. The solution was propylene carbonate, 1.0 M in LiBF₄. Deposition was effected in stirred solution at 25 mA cm⁻² for 60 sec., yielding 1500 mC cm⁻² of total cathodization. (Note: We use the phrase "total cathodization", rather than "total deposition" so as not to imply that the total current passed during cathodization is completely utilized in the electrodeposition of metallic lithium.) Anodizations were conducted at the current densities indicated and the resultant curves corrected for iR drop as discussed in the 1st Quarterly Report.

In Table 1 are shown the complete series of measurements obtained in this solution. Since, at currents of 75 mA cm⁻² or less the polarization was negligible, the potentials are not shown in the table.

Table 1
Anodic Utilization of Electrodeposited Lithium

Conditions of Deposition ^a i (mA cm ⁻²) x t (sec) = Q (mC cm ⁻²)			Anodic Discharge Current (mA cm ⁻²)	Anodic Utilization (%)
25	1200	30,000	100	36
50	600	30,000	100	34
25	1200	30,000	20	47
25	240	6,000	100	46
25	240	6,000	10	78

Table 1 (Con't)
Anodic Utilization of Electrodeposited I

Conditions of Deposition $i \text{ (mA cm}^{-2}) \times t \text{ (sec)} = Q \text{ (mC cm}^{-2})$			Anodic Discharge Current (mA cm ⁻²)	Anodic Utilization (%)
25	120	3,000	100	75
10	300	3,000	100	51
25	120	3,000	75	65
25	120	3,000	50	80
25	120	3,000	10	87
25	60	1,500	125	58
25	60	1,500	100	67
25	60	1,500	75	83
25	60	1,500	50	84

c. Discussion. In the past it has been generally observed that anodic utilization is not dependent on the current with which lithium is anodically stripped but is dependent on the conditions under which the lithium has been electrodeposited. The data shown in table 1 do not, in themselves, encompass a sufficiently wide range of experimental conditions to substantiate these observations. They do modify these previous observations in indicating that at sufficiently high anodic currents there is a decrease in utilization. The decrease in utilization commences at currents of 50-75 mA cm⁻². This is about the limiting current expected for a propylene carbonate solution, 1 M in supporting electrolyte.

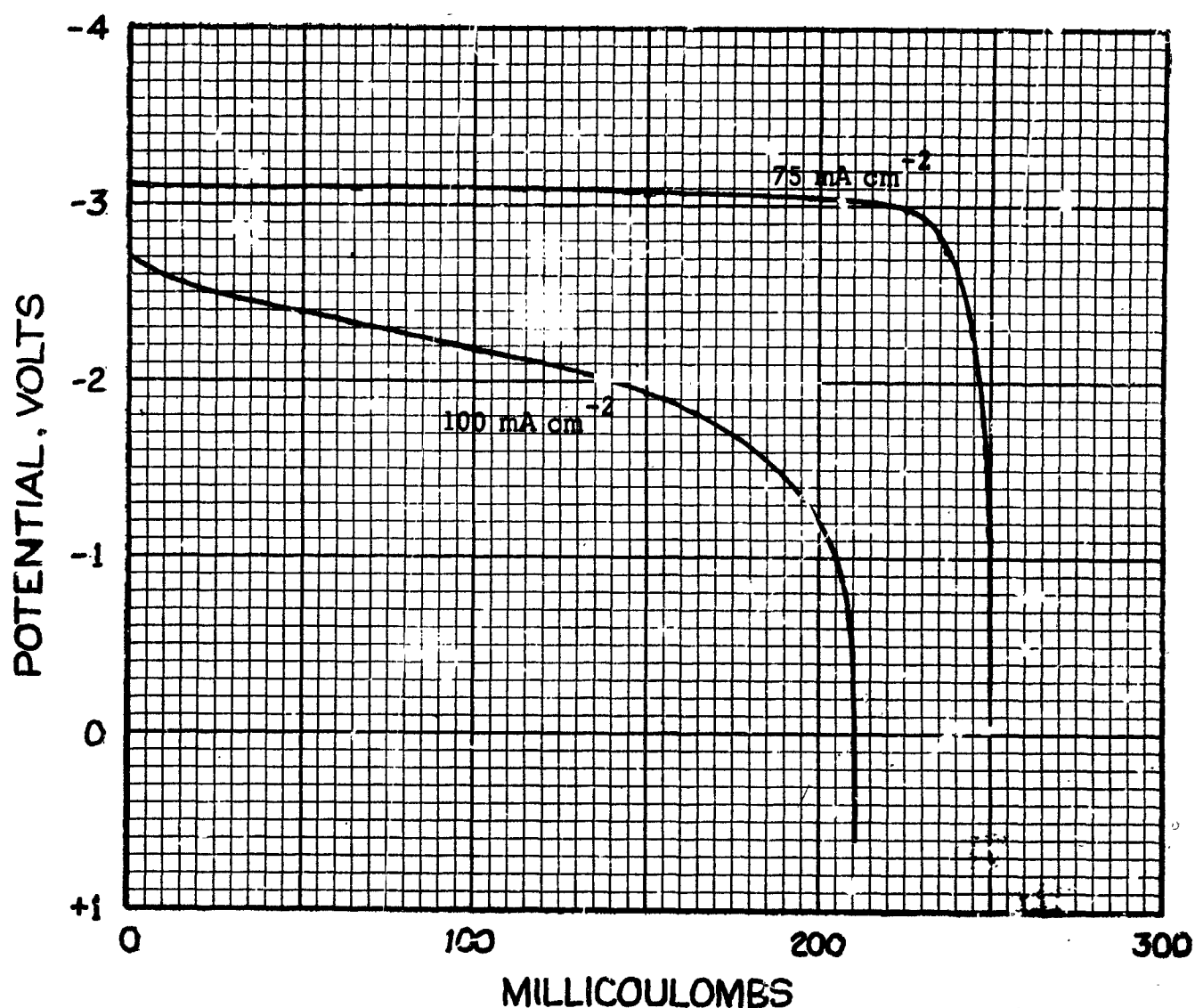


Figure 1: Anodic Discharge of Lithium.

Preceding cathodic deposition of lithium had been conducted at 25 mA cm^{-2} for 60 sec. (1500 mC cm^{-2}) in stirred solution. Anodic discharge conducted at current indicated in stirred solution. (Note: X-axis gives the actual charge for the 0.2 cm^2 electrodes, and should be multiplied by five to give the charge density.) Potentials have been corrected for iR drop and are given with respect to the silver disc reference electrode, against which the open circuit potential of the lithium electrode is -3.2 V .

The results are compared with those obtained by other groups. The group at Lockheed⁽¹⁾ has reported data obtained in propylene carbonate, 0.63 M in LiAlCl_4 , where 72% anodic utilization was obtained at 1 mA cm^{-2} (Total Cathodization = 180 mC cm^{-2}) decreasing to 30% utilization at 6 mA cm^{-2} (Total Cathodization = 900 mC cm^{-2}).

Rocketdyne⁽²⁾ has reported data obtained in propylene carbonate, 0.51 M in LiBr. Following cathodization at 9.65 mA cm^{-2} for 600 sec. (5800 mC cm^{-2}) the electrodeposited lithium was discharged at 4.825 mA cm^{-2} . Anodic polarization was negligible until, after 12 min., the sudden positive jump in potential signalled completion of discharge, yielding 60% anodic utilization.

The same group⁽³⁾ has reported data on the anodic utilization of bulk lithium metal electrodes, obtained by pressing lithium ribbon on nickel supports. Essentially 100% efficiency with little polarization was shown for discharges at 4 mA cm^{-2} which, for the amount of lithium initially present, corresponded to about a 10-hr. rate.

d. Conclusions. The results are best discussed with reference to the capacities of actual secondary cell electrodes. The capacity of a cell with flat plate construction will doubtless be determined by the capacity of the cathode. We believe that the development of a cathode with a capacity of $0.01 \text{ A-hr cm}^{-2}$ ($36,000 \text{ mC cm}^{-2}$), capable of operative at the one-hour rate (10 mA cm^{-2}) is a reasonable objective. A bulk lithium anode with this capacity would be a little less than 2 mils thick.

(1) Lockheed Missiles and Space Co., Technical Report AFAPL-TP-64-147, Feb. 1965.

(2) Rocketdyne, Fourth Quarterly Progress Report, June 1964.

(3) Rocketdyne, Second Quarterly Progress Report, December 1963.

We distinguish between anodic utilization and anodic efficiency. Anodic utilization is the total anodic current passed before polarization divided by the total cathodic current. Anodic efficiency is the fraction of anodic current actually used in the discharge of lithium.

Anodic efficiency may be low if the physical form of the deposit is such that preferential anodic attack at the base of the lithium metal severs electrical contact, or if passivating films form during anodization. Either difficulty should result in a dependence of efficiency on anodic current. Since, for the anodic dissolution of lithium electrodeposited under identical conditions, there is observed no marked variation in anodic utilization with the magnitude of the anodic current (except for very high currents, as discussed previously), and since, as shown in figure 1, no serious polarization ensues during anodization (except, again for very high currents) we believe that the anodic efficiency for the electro-dissolution of lithium to be inherently 100%. We have not yet attempted to discharge bulk lithium but such experiments will be done in the future and are necessary in order to definitely establish this fact.

At present it appears that low anodic utilization primarily reflects the degree to which the preceding cathodic deposition was efficient. Thus, an anodic efficiency of 85% indicates, we believe, that the preceding cathodization was only 85% efficient.

The failure to obtain satisfactory anodic utilization for deposits as large as $30,000 \text{ mC cm}^{-2}$, as indicated in table 1, is quite serious. It being our present conclusion that the anodization step itself is not the limiting process, attention in the following sections will be focused on the cathodization process.

3. Cathodic E vs. i measurements.

a. Experimental. Such measurements are obtained by applying constant current and measuring the resultant steady state electrode potential, or, alternatively, by holding the electrode potential constant and measuring the resultant steady state current. In the procedure followed to obtain the results shown in figures 2-6 lithium was first electrodeposited on the center silver disc reference electrode. It has been found that such an electrode exhibits a stable, reproducible potential over the period of time required for the experiments. The potential of the circumferential platinum disc electrodes was measured with respect to the center lithium reference electrode. Both potentiostatic and galvanostatic methods were employed, and the steady state conditions were those which obtained in stirred solution. Following completion of the cathodic run the amount of lithium metal actually deposited during the cathodization was determined by anodic discharge, it being assumed, as discussed in the preceding section, that anodic efficiency is 100%.

b. Results. The results of a series of experiments are shown in figures 2-6. The open circles in figures 2-5 represent the results of the steady state E vs. i measurements. The potentials were corrected for iR drop as described in the First Quarterly Report. The dashed line curves represent the current actually consumed in lithium reduction. The solid line curves represent the plots of $it^{1/2}$ vs. E and will be discussed in the following sections 4 and 5. Steady state conditions are not always obtained. This was particularly apparent in the 0.05 M solution, the results for which are shown in figure 6. In this figure the horizontal lines show the range of the potential variation observed when the electrode was cathodized at constant current.

c. Discussion. Attention is directed to the fact that the

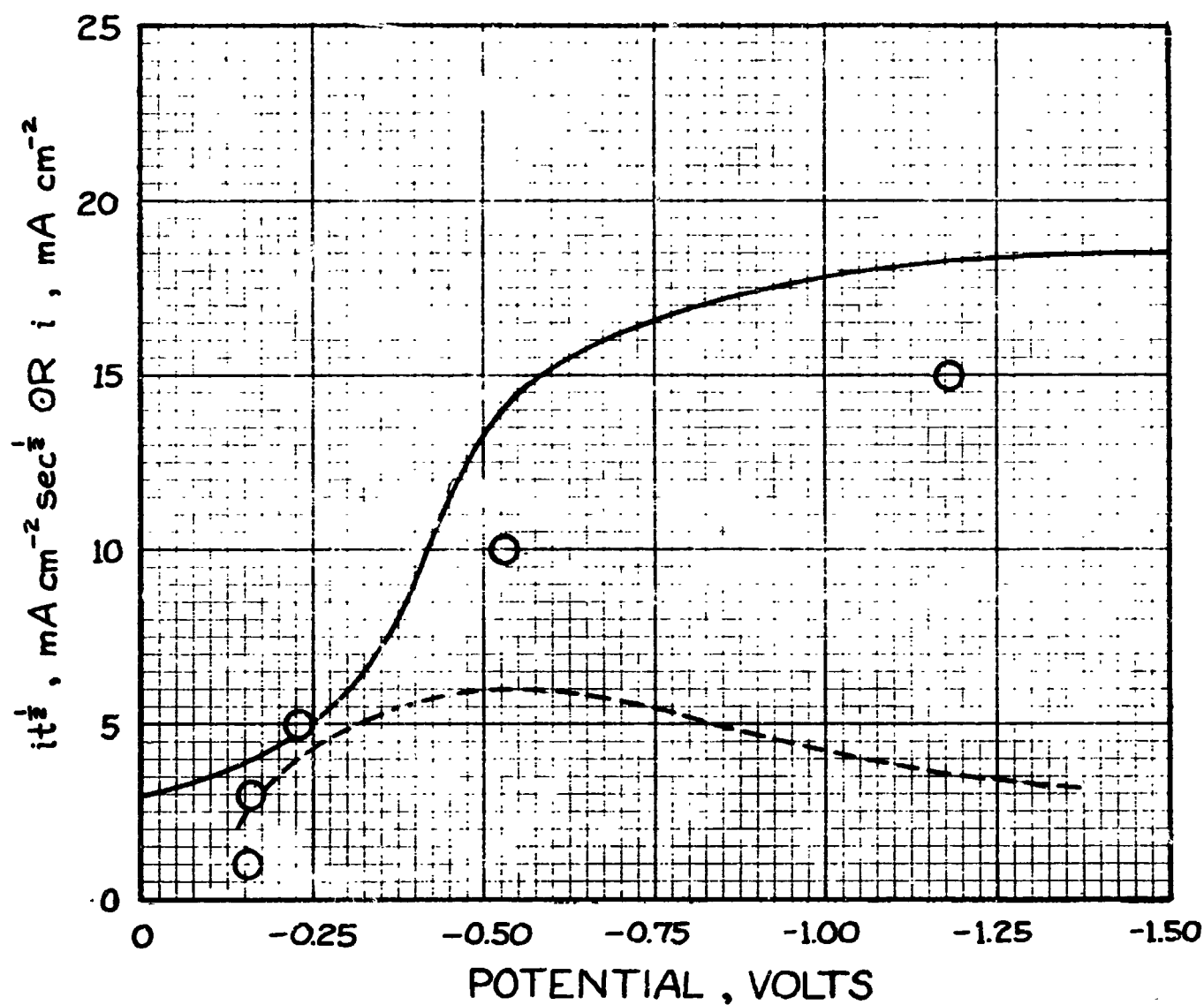


Figure 2: E vs. i -- 0.1 M LiBF_4 /Butyrolactone

Open circles are steady state E vs. i measurements. Dashed line is E vs. the actual current consumed in lithium reduction. Solid line is E vs. $i^{1/2}$, discussed on P. 18.

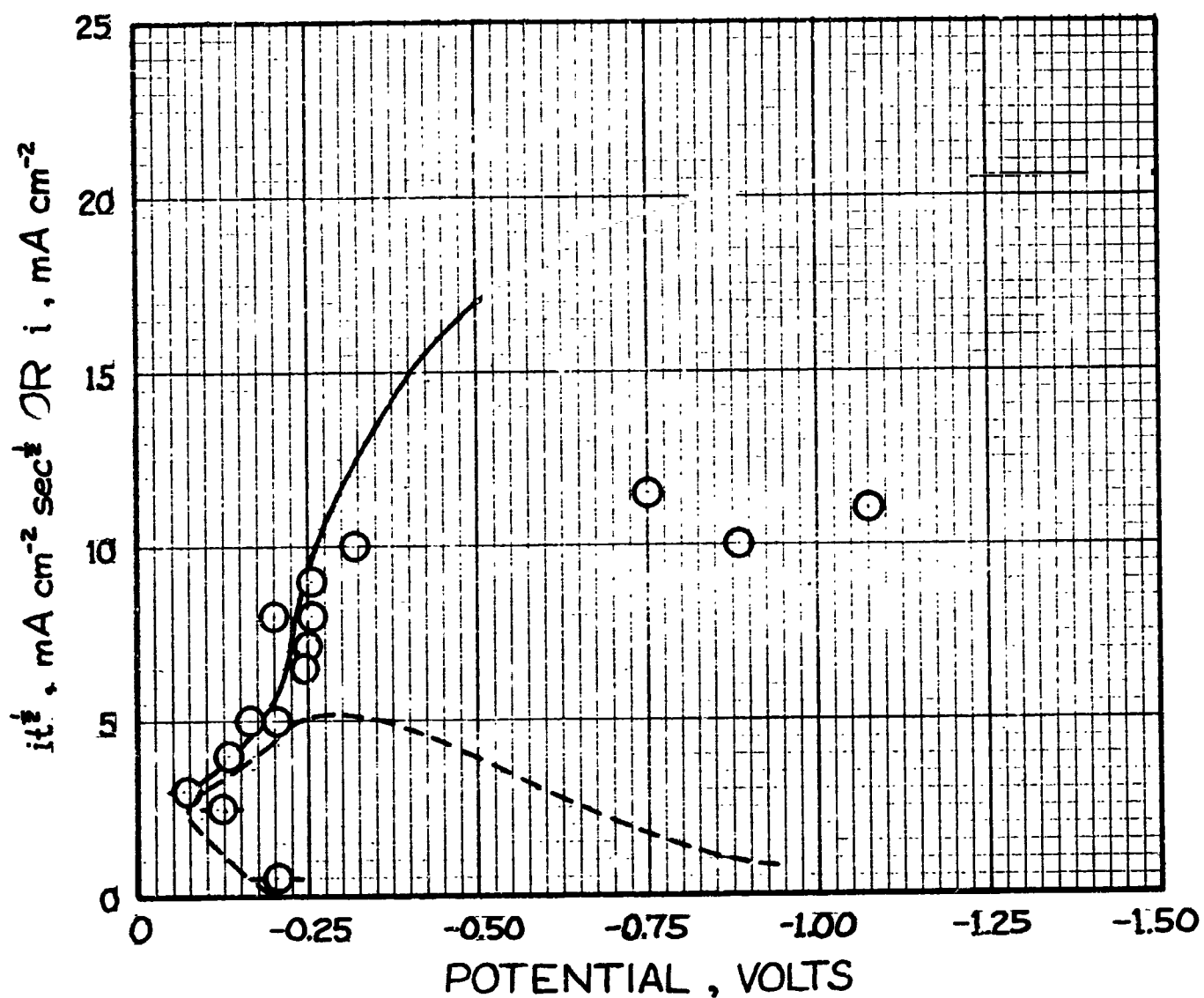


Figure 3: E vs. i -- 0.1 M LiClO_4 /Propylene Carbonate

Legend same as Figure 2, p. 8.

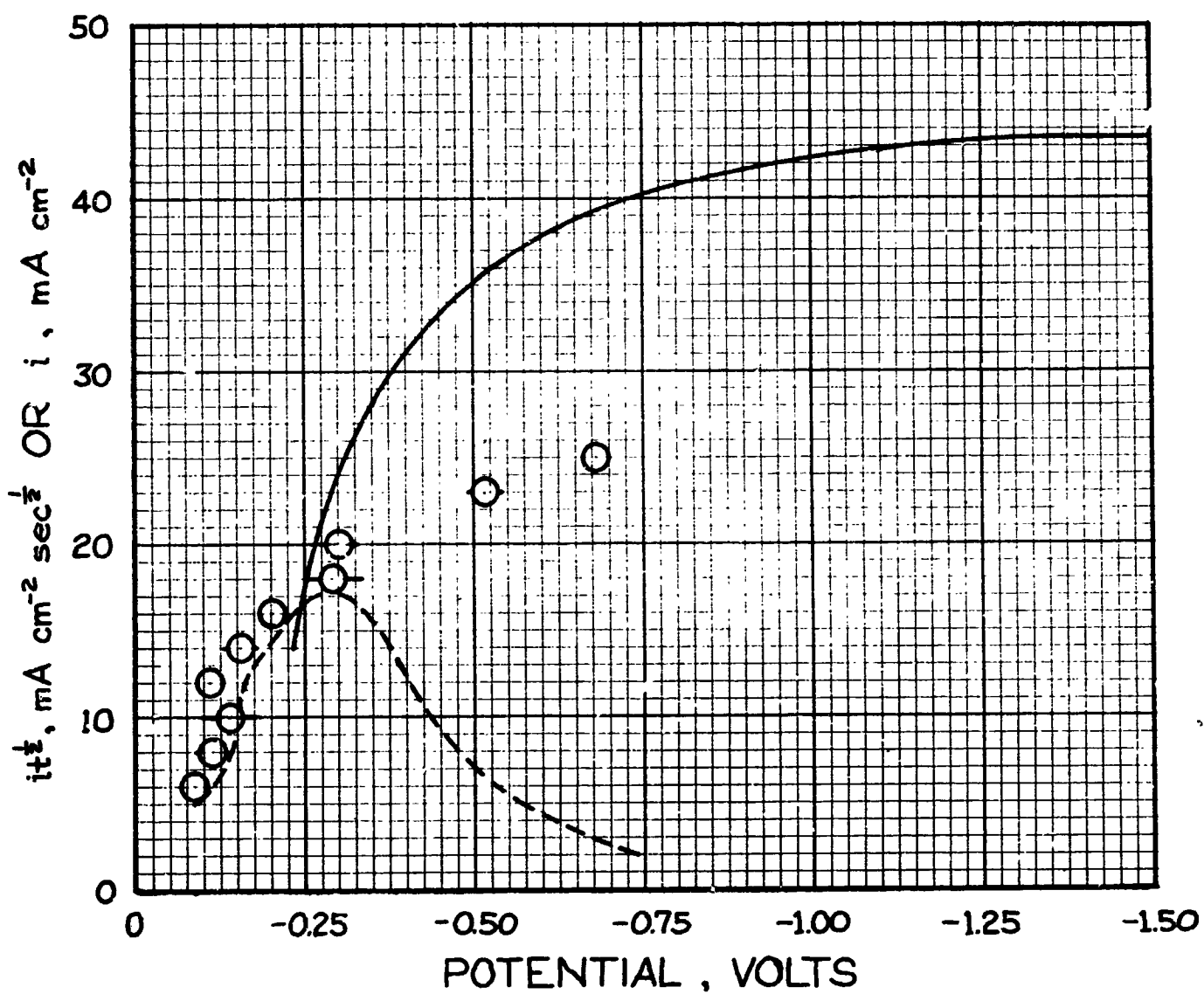


Figure 4: E vs. i -- 0.2 M LiClO_4 /Propylene Carbonate

Legend same as Figure 2, p. 8.

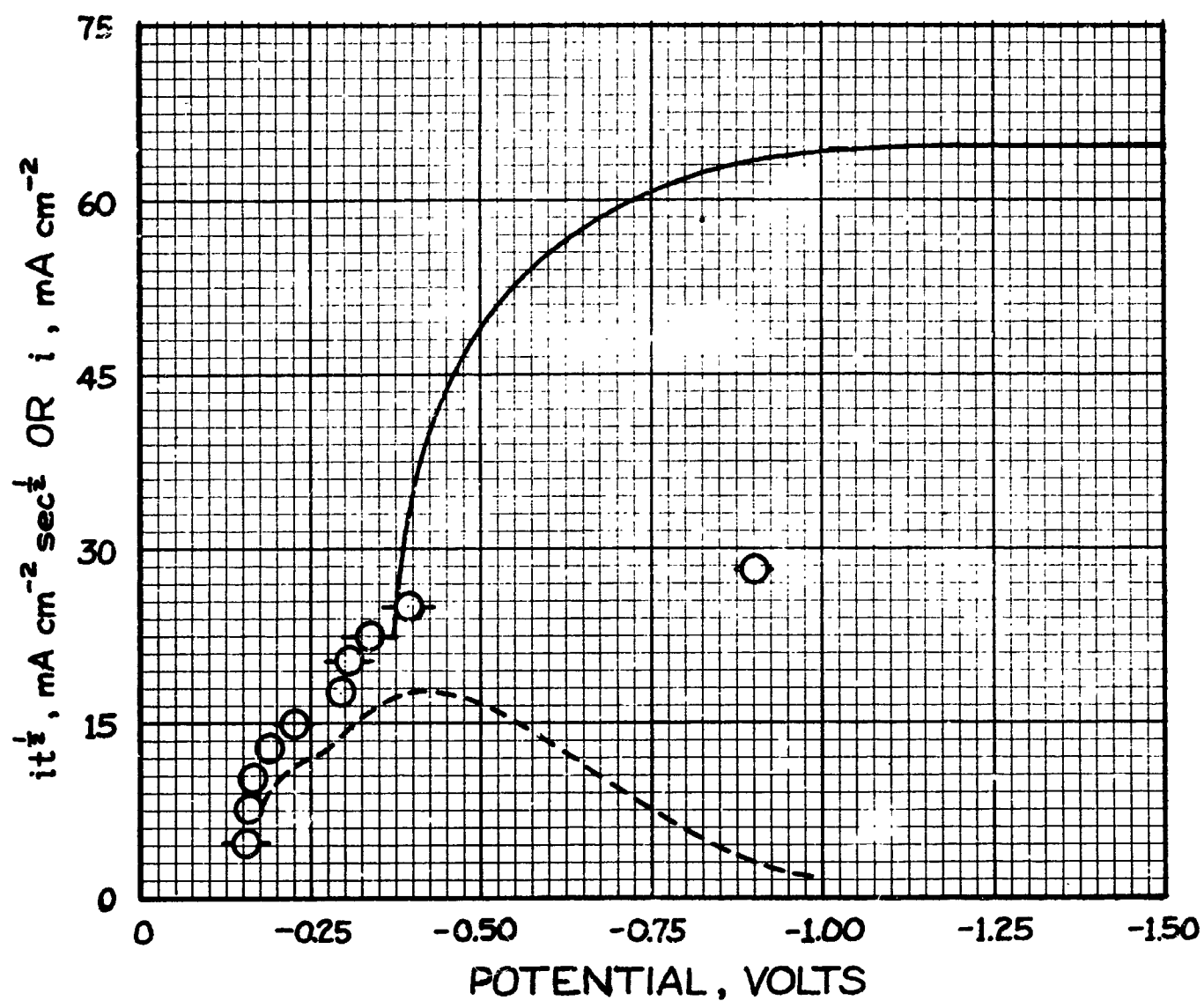


Figure 5. E vs. i -- 0.3 M LiClO_4 /Propylene Carbonate

Legend same as Figure 2, p. 8.

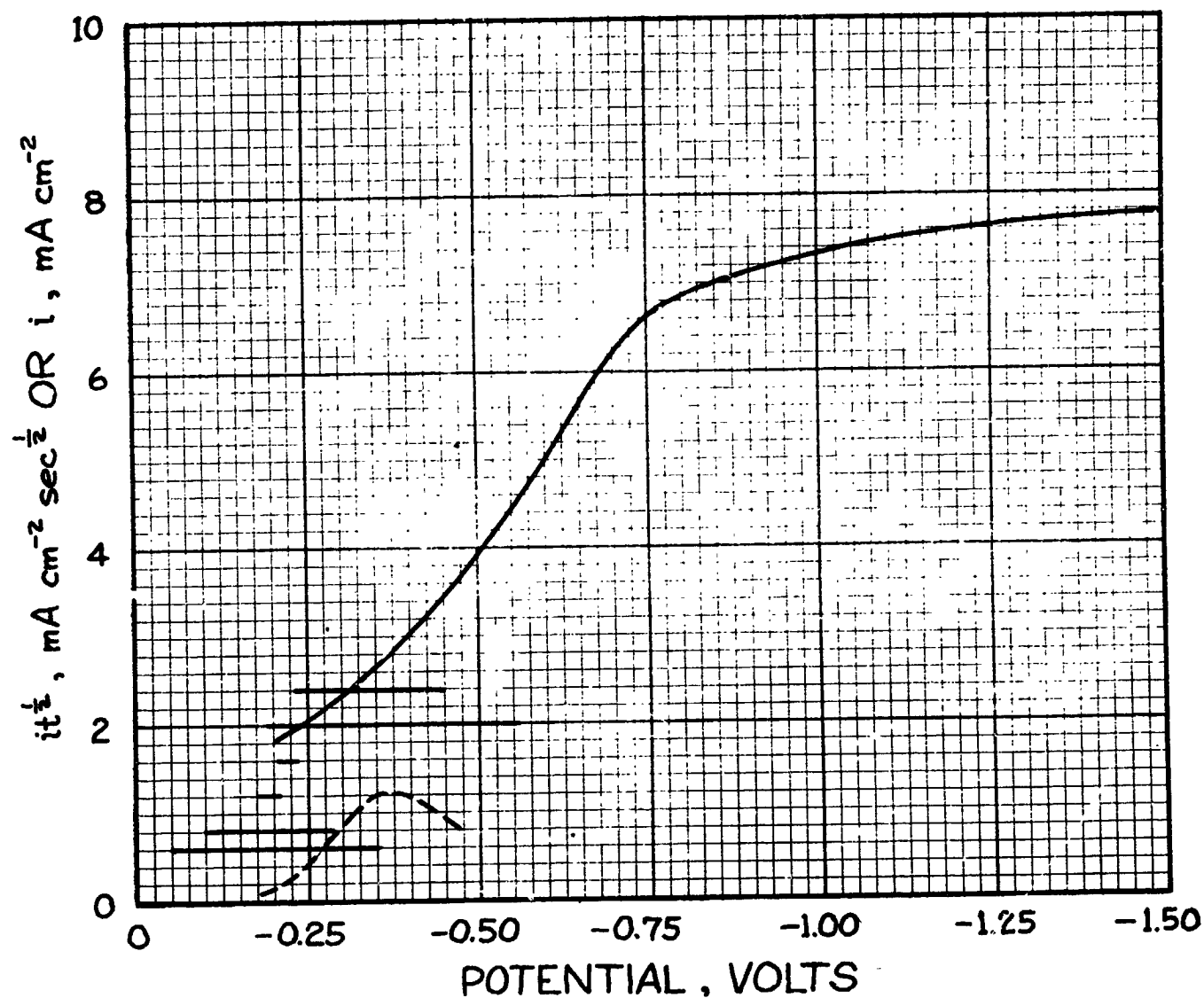


Figure 6: E vs. $1 - 0.05 \text{ M LiClO}_4/\text{Propylene Carbonate}$

Horizontal lines are results of measurements performed at constant current, and show observed potential variation. Dashed line is E vs. the actual current consumed in lithium reduction. Solid line is E vs. $it^{1/2}$, discussed on p. 18.

potentials are quite negative to the open circuit potential, indicating the reduction process is "irreversible". It is also noted that the actual current consumed in lithium reduction goes through a maximum. A qualitative explanation for this phenomena is developed below.

It is assumed that two cathodic processes may occur, and that both processes consume lithium ions though in different ways. It is necessary to postulate lithium consumption in both reactions in order to account for the fact that a proportionality between the concentration of lithium and $iT^{1/2}$ is observed, even though all of the current is not expended on lithium reduction. We assume the first reaction to be the reduction of lithium to the metal:



and the second reaction to be the reduction of some unknown material and one of the products of this reduction to be oxide ions. The reduction is assumed to be followed by the precipitation of lithium oxide at the electrode, thus resulting in the removal of lithium ions from solution.



To account for the fact that the current consumed in lithium reduction, reaction 1, diminishes with more negative potentials, we assume that reactions 1 and 2 may be represented by the Tafel plots shown in figure 7. It is emphasized that these plots have not been obtained from the data in figures 2-6 but are only intended to give a qualitative representation of the behavior displayed in these figures.

Curve a in figure 7 is the hypothetical Tafel plot for reaction 1, the reduction of lithium ions. This curve is described by the equation:

$$i = i_0 \exp(-nFE/RT) \quad (4)$$

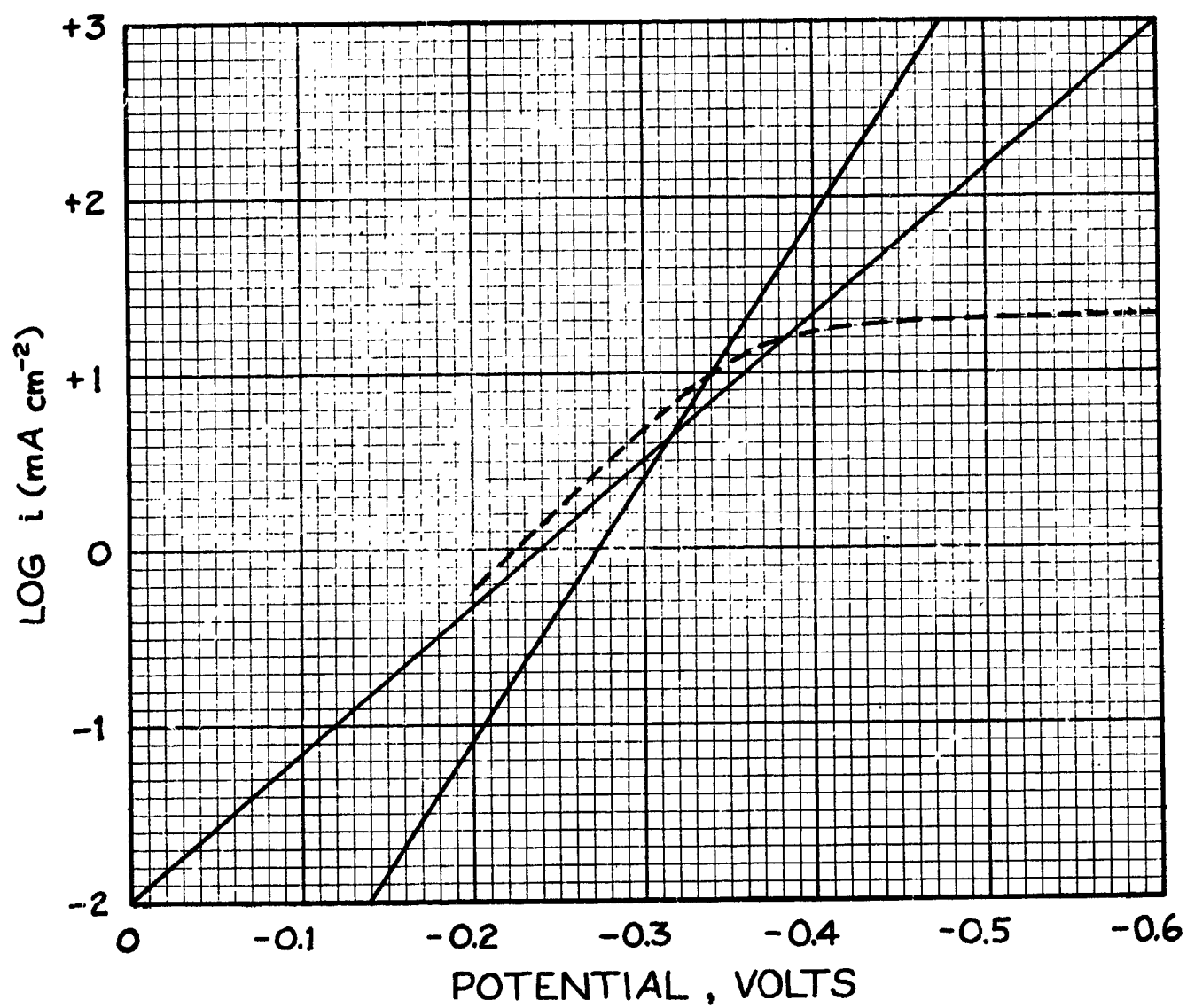


Figure 7: Hypothetical E vs. log i curves for Cathodization.

where i_0 is the exchange current, E the potential versus the open circuit potential of the lithium electrode in the same solution, and α is the transfer coefficient. Alternatively, one may write:

$$E = \frac{0.059}{n} (\log i_0 - \log i) \quad (5)$$

Curve a is drawn using a value of 0.01 mA cm^{-2} for the exchange current and 0.5 for the transfer coefficient, giving a Tafel slope of 0.118 V.

Curve b is the hypothetical Tafel plot for reaction 2. The curve is described by the equation:

$$E = -0.275 - 0.067 \log i. \quad (6)$$

At this point it is important only that the two Tafel slopes should cross, and curve b was quite arbitrarily drawn with this in mind.

Thus far no consideration has been given to the effects of concentration polarization. This will now be discussed. The net E vs. $\log i$ curve cannot be obtained from simple addition of the currents for the two reactions at a given potential, since reaction 1 is dependent on the concentration of lithium ions at the electrode surface. Reaction 1 is more accurately described by:

$$i = i_0 \frac{C}{C_0} \exp(-\alpha nFE/RT) \quad (7)$$

where C is the concentration at the electrode surface, and C_0 is the bulk concentration of lithium ions. C/C_0 is equal to $(1 - i/i_D)$, where i_D is the limiting current, and i is the total current, since both reductions result in consumption of lithium ions through reactions 1 and 3.

Using a value for the limiting current of 20 mA cm^{-2} one may write:

$$E = 0.118 (\log i_0 - \log i + \log (1 - i/20)) \quad (8)$$

The net $\log i$ vs. E curve is calculated from equations 6 and 8. This curve, however, must be further corrected for the potential gradient existing across the diffusion layer. As discussed in the First Quarterly Report this

potential is given by:

$$E_{R-diff} = 0.06 \log (1 - i/i_D) \quad (9)$$

The potential so calculated must be added to the potentials for the net $\log i$ vs. E curves obtained from equations 6 and 8. The final net $\log i$ vs. E curve so calculated is shown by the dashed line in figure 7. The i vs. E curve so calculated is shown by the solid line in figure 8. The dashed line in figure 8 is the calculated current actually used in lithium reduction.

d. Conclusions. Electrochemical measurements performed in propylene carbonate solutions of lithium salts indicate that the mechanism of cathodic reduction is complex. The observed results may be qualitatively explained by postulating two competing reduction processes, both consuming lithium ions but only one of which consumes lithium ions through the formation of lithium metal.

4. Cathodic E vs. t measurements (chronopotentiograms)

a. Experimental. Such measurements are made by applying constant current to the working electrode in quiet solution and measuring the subsequent variation in potential with time.

b. Results. Chronopotentiometric measurements have been discussed in detail in previous reports, issued since the beginning of our work. Under ideal conditions chronopotentiograms should convey the same information as do polarization curves (i.e. E vs. i curves). The advantages of chronopotentiometry lie in the fact that less time is required for a series of measurements and that, since the current is held constant, simple corrections for iR drop can be made. Further results of chronopotentiometric measurements will be discussed in the following sections.

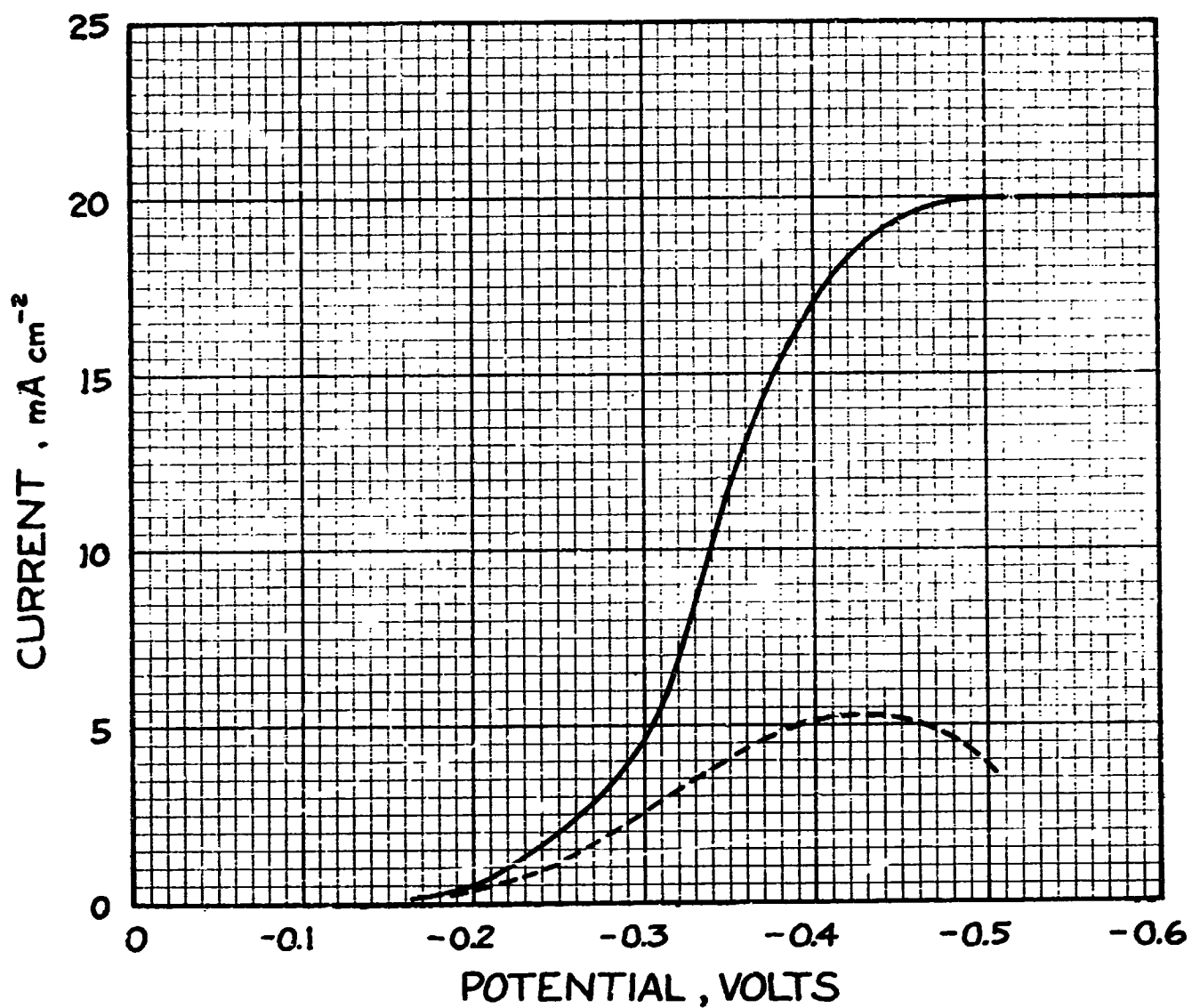


Figure 8: Hypothetical E vs. i curves for cathodization.

5. Cathodic E vs. $it^{1/2}$ measurements.

a. Experimental. Such measurements are made by replotting the data obtained from the chronopotentiograms and do not, in themselves, constitute a different technique of measurement. The potentials at various times after the commencement of electrolysis are first corrected for iR drop and then plotted against the product of the current and the square root of the time at which the potential obtains. Obviously, as many different points can be taken as desired to clearly define the full E vs. $it^{1/2}$ plot.

b. Results. In figures 2-6 the solid line curves are plots of E vs. $it^{1/2}$ obtained from chronopotentiograms. The curves have shapes similar to the more conventional polarization curves or polarograms and, as discussed in the First Quarterly Report, such plots are, indeed, directly analogous to steady state E vs. i curves. A plateau is observed at more negative potentials. This plateau is $iT^{1/2}$ where T is the transition time. It will be observed that, at lower values of $it^{1/2}$ the full curve has not been drawn. This is because chronopotentiograms had not been obtained at sufficiently low currents to define the curve in this region.

c. Discussion. E vs. $it^{1/2}$ curves offer a concise and efficient means for the presentation of data and will be extensively used in the remainder of this report and in succeeding reports.

C. Electrochemical Characterization of Electrolytes.

1. Effects of Solvent Purification Procedures.

a. Experimental. Solvents have been routinely purified by vacuum distillation. The apparatus consists of a 90-cm, jacketed, electrically heated column packed with Berl saddles and fitted with a water jacketed receiver. Distillations are normally conducted at 1-2 mm. Hg at a reflux ratio of 1:1. About three liters of solvent are placed in the pot and the still is operated at total reflux until the pressure and temperature become

constant. For propylene carbonate distilling at 1 mm Hg the temperature at the head is about 65°C . and the pot temperature is about $130\text{--}150^{\circ}\text{C}$. The initial 200–300 ml. of distillate are discarded and the remaining distillate is collected in 1000-ml. flasks. About 300 ml. of solvent are left in the pot and discarded.

To examine the electrochemical effects of distillation the initial distillate was not discarded, and successive 100-ml. fractions were collected and examined as described in the next paragraph.

A cell was fabricated from glass tubing about 1.5 in. in diameter and 6 in. long. A stopcock was attached to the bottom of the cell through which argon could be bubbled through the solution. Before each experiment the cell was rinsed with distilled water and acetone and baked at 140°C . After removal from the oven the argon flow line was immediately attached to the stopcock at the base of the cell and argon was allowed to flow through the loosely stoppered cell until it had reached room temperature. A 50-ml. sample of the 100-ml. distillate fraction was poured into the cell and deaerated for at least twenty minutes. An amount of solid LiClO_4 was then added to the solution to give a final concentration of 0.1 M l^{-1} . In the cell were placed a platinum wire helix counter electrode and a lollipop type electrode of the type previously described. In the results here described polished platinum disc electrodes were employed, each 0.2 cm^2 in area. The electrode assembly was polished with one-micron alumina, thoroughly rinsed with distilled water, then acetone and dried under a stream of warm air. The electrodes were then wiped with ordinary tissue before immersion in the solution.

c. Results. Typical results are shown in figures 9–13 and discussed below.

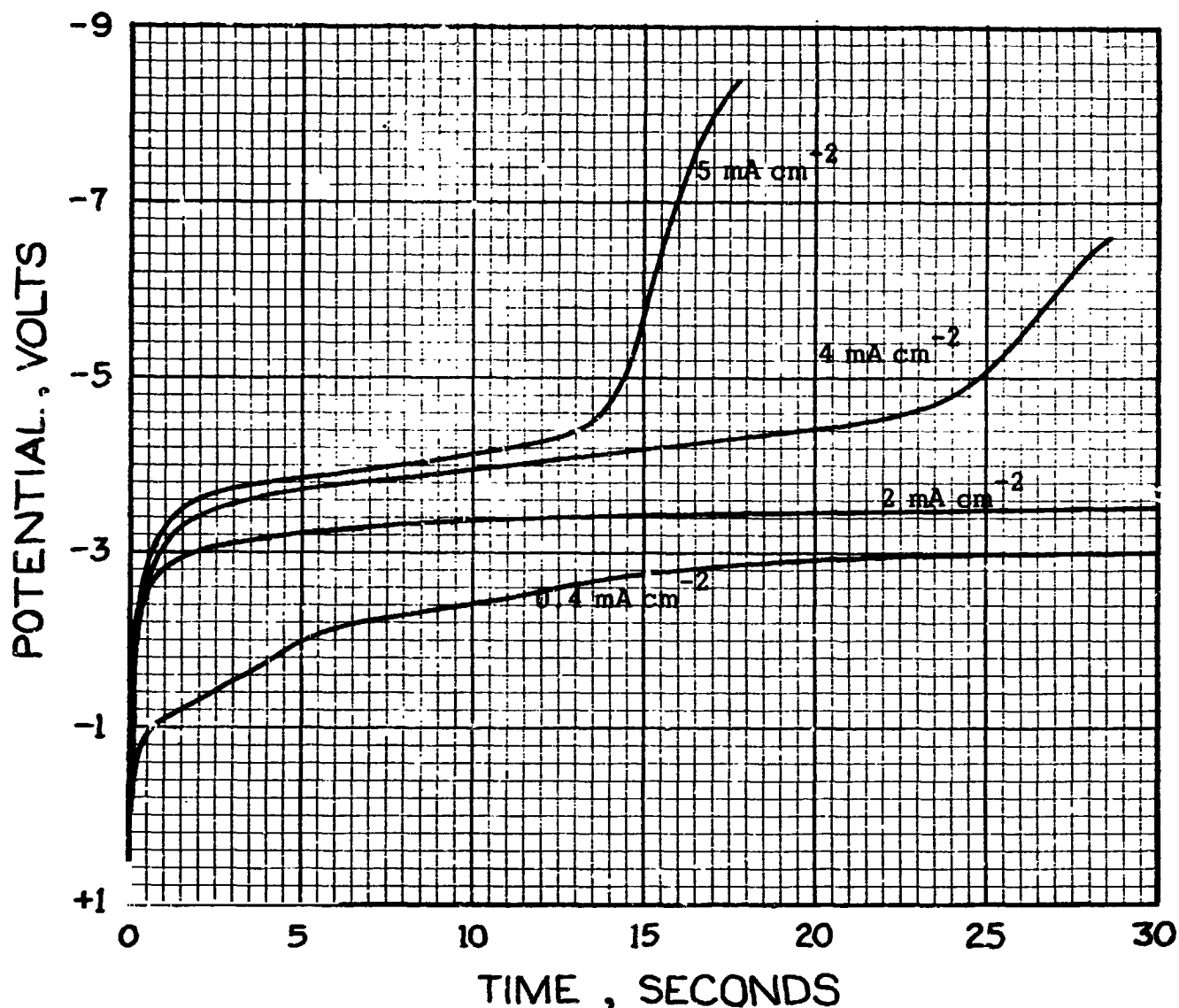


Figure 9: Examples of Typical E vs. t curves for Cathodization.

Curves obtained on polished platinum disc electrodes at current densities indicated. Potentials, corrected for iR drop, are given with respect to a silver disc reference electrode, against which the open circuit potential of the lithium electrode is about -3.0 V. The solution was fraction 3 of the vacuum distilled propylene carbonate, made 0.1 M in LiClO_4 .

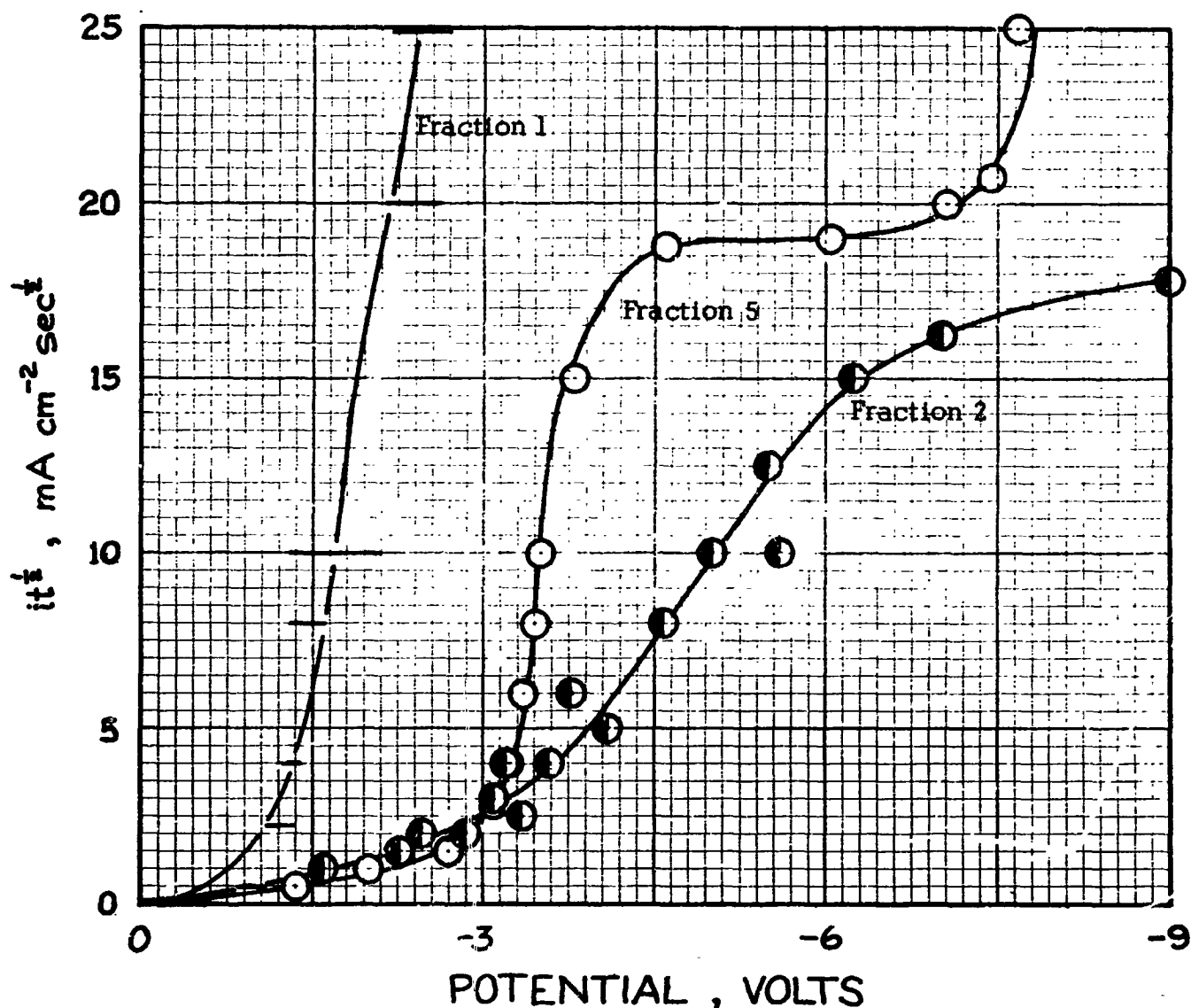


Figure 10: Examples of Typical E vs. $it^{1/2}$ curves for Cathodization.

Results obtained by plotting data from chronopotentiograms obtained in fractions 1, 2, and 5 of propylene carbonate, Each solution was 0.1 M in LiClO_4 . Potentials, corrected for iR drop, are given with respect to the silver disc reference electrode, against which the open circuit potential of the lithium electrode is about -3.0 V.

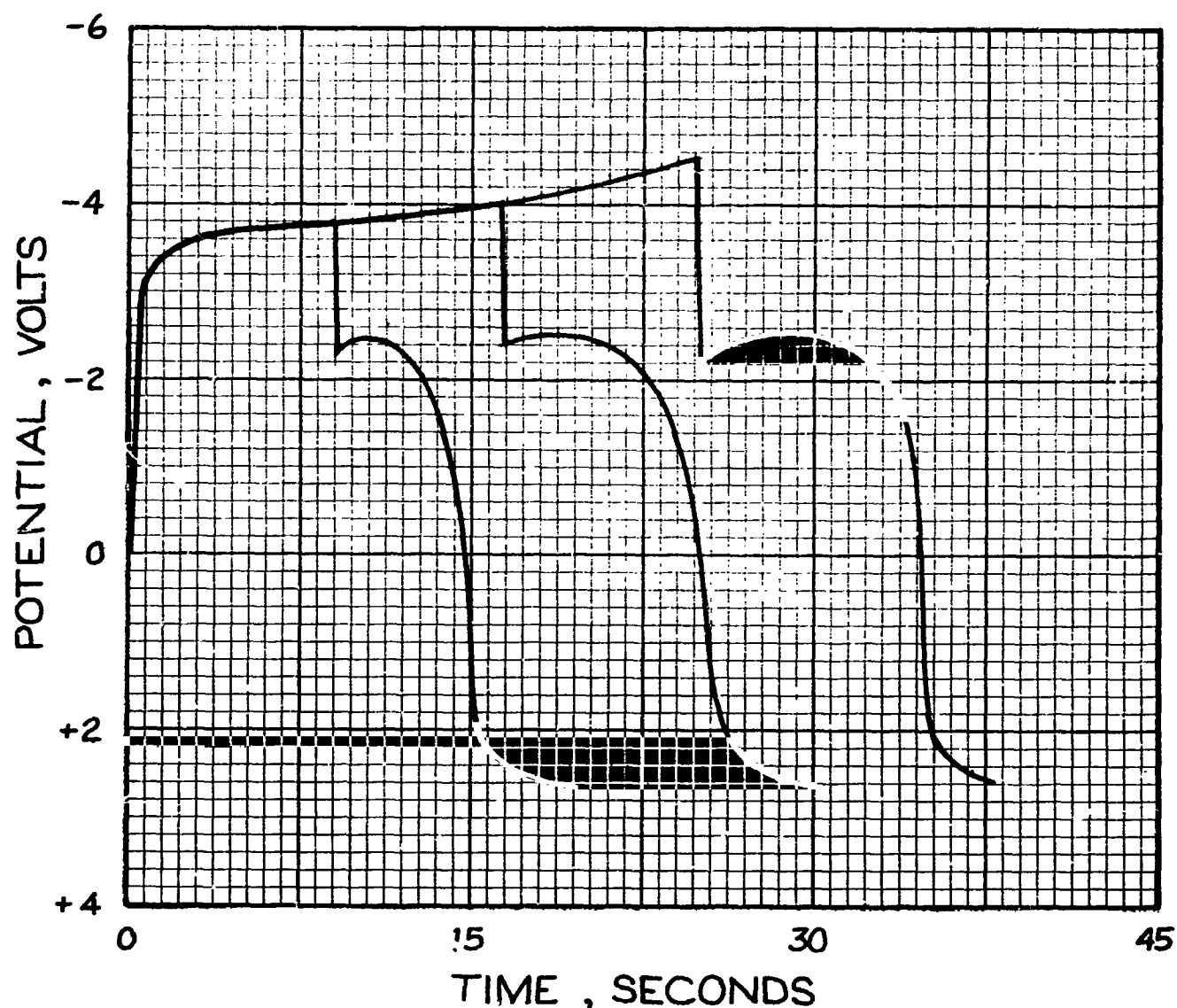


Figure 11: Examples of Typical E vs. t curves with Current Reversal.

Results obtained in fraction 3 of vacuum distilled propylene carbonate, made 0.1 M in LiClO_4 , at 4 mA cm^{-2} . Potentials have not been corrected for iR drop, and are given with respect to the silver disc reference electrode.

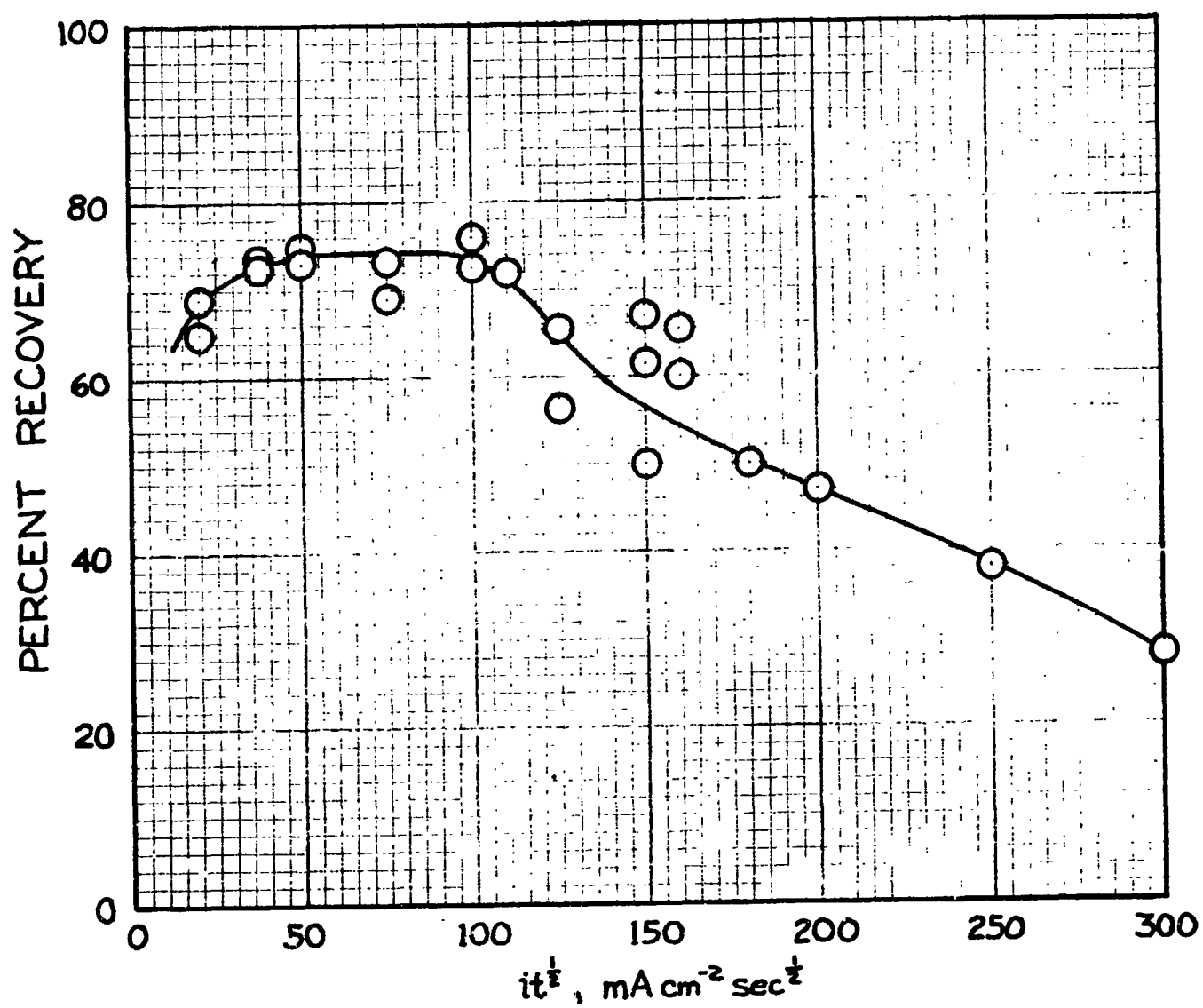


Figure 12: Recovery vs. $it^{1/2}$ Curves -- 1.0 M LiClO_4 /Propylene Carbonate

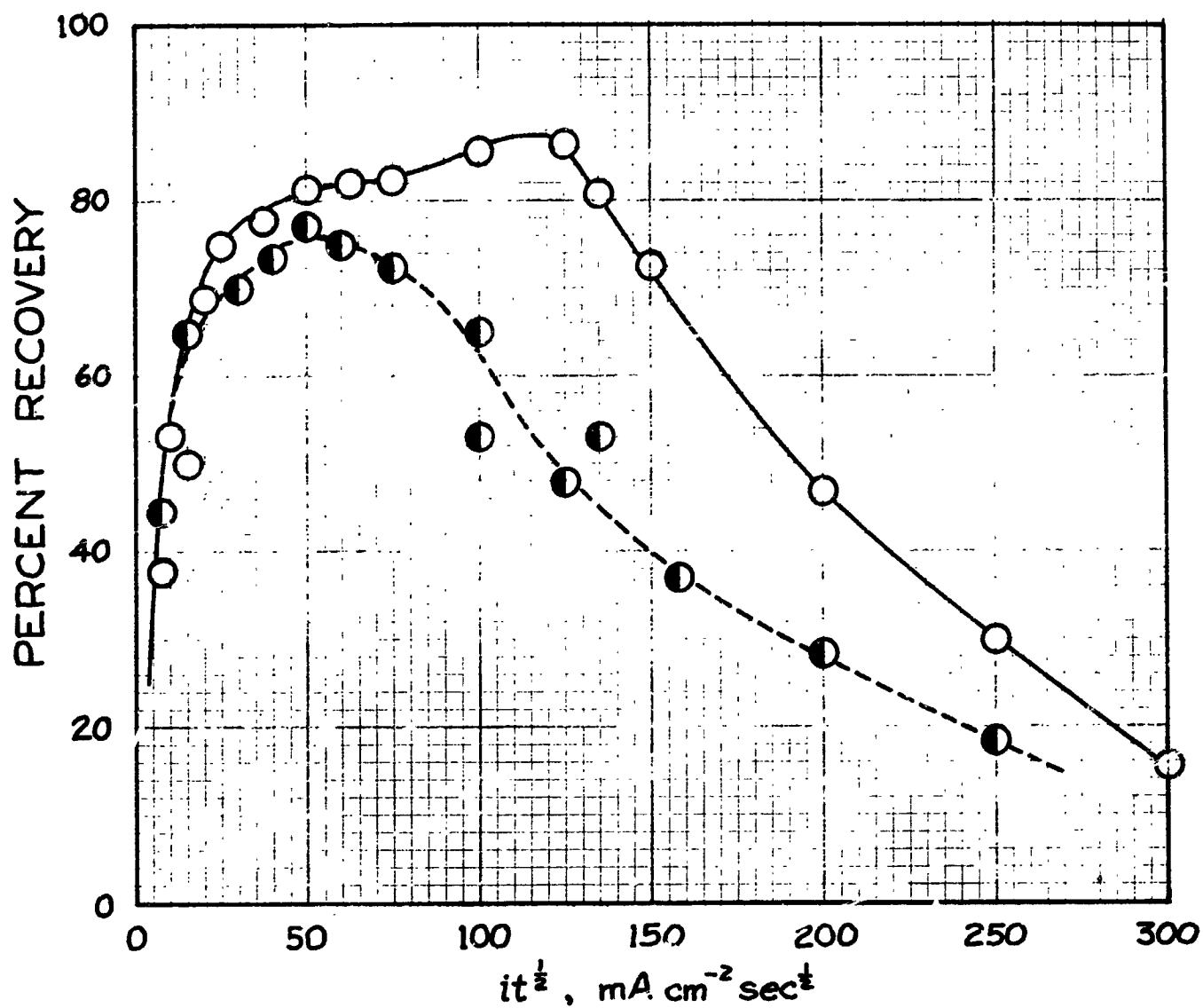


Figure 13: Recovery vs. $it^{1/2}$ Curves -- 1.0 M LiBF_4 /Propylene Carbonate
 Open circles show results obtained in fraction 7; semi-closed circles show results obtained in fraction 2.

d. Discussion:

(1) Figure 9: In each fraction a series of chronopotentiograms were obtained as shown in figure 9.

(2) Figure 10: From the series of chronopotentiograms were obtained data for plotting E vs. $it^{1/2}$. Typical plots are shown in figure 10. Fractions 3-7 all gave plots essentially identical to that shown in figure 10 for fraction 5 and are thus not shown. Fraction 1 gave no evidence of lithium reduction and gassing occurred immediately on the commencement of cathodization. Fraction 2 yielded a sometime ill-defined transition time as can be seen from the approach toward an $it^{1/2}$ plateau.

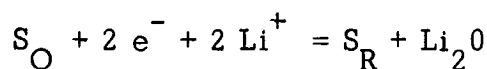
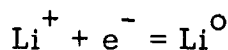
(3) Figure 11: Plots of E vs. $it^{1/2}$ alone did not yield all the desired information and chronopotentiograms were run in which, after a certain period of time, the current was reversed. Typical results are shown in figure 11.

(4) Figure 12: It was found useful to characterize the system by using chronopotentiometry with current reversal as described in paragraph (3) above, and by plotting the measured anodic utilization versus the value of $it^{1/2}$ at which the current was reversed. In figure 12 are shown results obtained in 1.0 M LiClO_4 . Such results give a quick assessment of the ability of the electrolyte to support lithium reduction. It will be observed that the efficiency decreases at $it^{1/2} = 100\text{--}150 \text{ mA cm}^{-2} \text{ sec}^{1/2}$. This is about the value of $it^{1/2}$ expected for lithium reduction in a propylene carbonate solution of this concentration.

Extensive measurements of $it^{1/2}$ vs. recovery were not made for the more dilute solutions since a few preliminary runs indicated that the general character of the curves was identical to that shown in figure 12. A maximum recovery plateau of between 70 and 80% was observed for fractions 5-7, for the 0.1 M LiClO_4 solutions, and a decrease in recovery was observed for values of $it^{1/2}$ larger than $20 \text{ mA cm}^{-2} \text{ sec}^{1/2}$, the $it^{1/2}$ of a 0.1 M

LiClO₄ solution.

(5) Figure 13: Figure 13 shows the results obtained in 1.0 M LiBF₄. The salt was synthesized as later described in this report. The open circles show the results obtained in fraction 7. The dotted line connects results obtained in fraction 2. It will be observed that, at lower values of $it^{1/2}$, the recoveries are quite similar. The major differences in efficiency are observed at the higher values of $it^{1/2}$. In section A-3, above, it was postulated that two reductions occur:



both of which consume lithium ions, though in different ways. We do not know what S_O might be -- possibly oxygen, water, carbon dioxide, or solvent. If the kinetic discussion presented in section A-3 is reasonably accurate the results shown in figure 13 suggest, we believe, that S_O, a species reduced with only slightly greater difficulty than lithium, is removed by distillation. Alternatively, S_O may be a species generated in solution through the catalytic action of impurities, largely removed by distillation.

d. Conclusions. The results described in this section demonstrate, we believe, the necessity for solvent purification in obtaining reasonable efficiencies for lithium deposition. At the same time, they show that routine vacuum distillation is not alone efficacious in improving lithium deposition efficiency. Plots of $it^{1/2}$ vs. E and percent recovery vs. $it^{1/2}$ are simple and meaningful expressions of the electrochemical characteristics of the system and will be extensively employed in future work in solvent purification and in assessing the relative merits of other electrolyte systems.

2. Further Examination of Solvent Purification Procedures.

a. Experimental. Two other procedures were investigated in an attempt to improve the purity of propylene carbonate.

(1) 3 liters of propylene carbonate were allowed to stand in contact with freshly cut sodium for one day prior to distillation.

Distillation was performed in the usual fashion, and the first 200 ml. of distillate were discarded. A portion of the remaining fractions was made 0.1 M in LiClO_4 and the solution examined by obtaining plots of $it^{1/2}$ vs. percent recovery.

(2) 3 liters of propylene carbonate were mixed with 50 ml. of benzene. It was thought possible that the water-benzene azeotrope could be initially distilled off to effect more efficient removal of water from the propylene carbonate. This was not successful as indicated by the fact that at temperatures as high as 100°C , at atmospheric pressure, a negligible amount of distillate was obtained. Thereafter, vacuum distillation was performed until the temperature and pressure at the distilling head were those normally obtained for the distillation of propylene carbonate. Successive fractions were then collected, made 0.1 M in LiClO_4 and examined by obtaining plots of $it^{1/2}$ vs. percent recovery.

b. Results. Plots of $it^{1/2}$ vs. recovery were prepared and their appearance was similar to those shown in figures 12 and 13. Maximum recovery was low in both purification procedures. In procedure a-1 above fraction 1 had a maximum recovery of 25% at $it^{1/2} = 15 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ this increased to 43% in fraction 6 at $it^{1/2} = 20 \text{ mA cm}^{-2} \text{ sec}^{1/2}$. In procedure a-2 above, fractions 1-3 gave no lithium deposition. Maximum recovery was obtained in fraction 6 and was then only about 47%.

Polarograms were obtained with the dropping mercury electrode for a number of the solutions and normally yielded well-defined lithium waves.

A small diffusion current plateau was normally observed before the lithium wave and its height was only about 1% that of the lithium diffusion current.

c. Conclusions. The electrochemical behavior of the lithium electrode has been used to assess the efficacy of two reasonable modifications in the procedure for purification of propylene carbonate. The results did not indicate improved purification of propylene carbonate: to the contrary, the electrochemical character of the solvent as described by $it^{1/2}$ vs. recovery curves for lithium was worse in both cases than when solvent was vacuum distilled directly.

3. Examination of Solute Synthesis Procedures.

a. Experimental. In the past, solutions of LiCl and LiClO_4 have been prepared directly from the commercially available salts. Solutions of LiAlCl_4 have been prepared in a variety of ways as described in preceding reports. Preparation through the direct addition of LiCl and AlCl_3 to propylene carbonate have not been satisfactory because of the catalytic decomposition of solvent by AlCl_3 . Variations such as cooling the solvent and adding the salts more slowly have improved the electrochemical quality of the electrolytes to some degree but the presence of deleterious decomposition products remains evident. During this quarter other synthetic procedures have been employed as described below. Preparation of solutions of LiBF_4 from the commercially available salt have not been satisfactory. The solutions exhibit a well-defined background reduction at about +2.5 V versus the lithium electrode. The $it^{1/2}$ for this background reduction is about that of a 0.02 M solution of a lithium salt. During this quarter other synthetic procedures have been developed as described below.

(1) Preparation of LiAlCl_4 . The most satisfactory results to date have been obtained by simply fusing LiCl and AlCl_3 together in a closed container on a hot plate, after which solvent was directly added to

the fused mixture. Solutions were prepared using various initial ratios of LiCl to AlCl_3 . As long as the initial ratio was 1:1 or greater ($\text{LiCl}:\text{AlCl}_3$) maximum recoveries of 70% were obtained in both propylene carbonate and butyrolactone as obtained from plots of recovery versus $i^{1/2}$. Solutions with a greater proportion of AlCl_3 showed diminished anodic utilization, about 50% maximum when the amount of AlCl_3 was twice that of LiCl.

(2) Preparation of $\text{LiBF}_4 \cdot \text{BF}_3$ etherate obtained commercially was first purified by vacuum distillation. To 150 ml. of the distillate were added 26 g. of anhydrous LiF. A salt suspension is obtained and is refluxed under nitrogen until the consistency of the suspension thickens. The mixture is then cooled, and the salt washed with excess ether to remove the unreacted BF_3 etherate and is then dried in a stream of nitrogen. The resultant colorless salt dissolves smoothly in propylene carbonate and butyrolactone without evidence of solvent decomposition. This salt was used for the results reported previously in this report.

b. Results. The efficacy of synthetic procedures for preparation of complex lithium salts has been determined through examination of the electrochemical behavior of the lithium electrode in solutions prepared from the synthesized material, see figure 13.

c. Conclusions. Complex salts of lithium catalyze solvent decomposition when significant concentrations of free Lewis Acid exist. Decomposition may be extensive and data based on solutions prepared from commercial materials or by the direct combination of the simple salts must be treated with extreme reservation.

II. THE COPPER ELECTRODE

A. Introduction.

A secondary cell cathode is not satisfactory if the cathode salt is too soluble. From the standpoint of weight and reversibility copper salts would appear to be the best candidates for secondary cell cathodes. During this quarter preliminary investigations of the solubility of copper salts in various electrolytes have been undertaken. This has led to a more detailed examination of the mechanism of copper reduction in chloride media and the solubilization of copper salts in chloride media as well as the solubilization of copper salts by impurities. Brief examination of the electrochemical behavior of sintered copper fluoride electrodes has been undertaken.

B. Solubility of Copper Salts.

1. Preliminary Screening Experiments.

a. Experimental. Forty-eight systems were examined, each comprising one solvent, one lithium salt, and one copper salt. The four solvents examined were propylene carbonate, butyrolactone, dimethylformamide, and tetrahydrofuran. The four lithium salts used were LiCl , LiClO_4 , LiAlCl_4 , and LiBF_4 . The three copper salts used were CuCl , CuCl_2 , and CuF_2 .

To 50 ml. of solvent were added an amount of solid lithium salt such that the concentration, if totally soluble, would be 0.1 M. An amount of copper salt was added such that the concentration, if totally soluble, would be 0.05 M. The solutions were tightly stoppered and allowed to equilibrate for at least a week, with frequent agitation. The solutions were then examined as described below.

b. Results:

(1) Visual Examination: The color of the solutions reflected the nature and concentration of the soluble copper species.

Solutions of copper (II) in the presence of chloride are deep red-orange to pale yellow, depending on the concentration of copper (II) and the concentration of chloride. Solutions of copper (I) are colorless when no copper (II) is present. Solutions of CuF_2 in LiBF_4 and LiClO_4 , wherein chloride is absent, vary in color from yellow green to pale blue.

(2) Conductivity Measurements: The results of the conductivity measurements are shown in table 2 below. The numbers shown in the table are the measured specific conductances.

Table 2
Conductivities of Copper-salt-lithium salt Solutions

Salt Combination	Solvent Conductivity (ohm ⁻¹ cm ⁻¹)			
	propylene carbonate	butyro- lactone	dimethyl- formamide	tetrahydro- furan
LiCl/CuCl	11.5×10^{-4}	16.0×10^{-4}	39.7×10^{-4}	2.5×10^{-4}
$\text{LiCl}/\text{CuCl}_2$	12.4 "	14.8 "	32.3 "	2.1 "
LiCl/CuF_2	7.2 "	7.9 "	14.9 "	0.4 "
$\text{LiClO}_4/\text{CuCl}$	17.8 "	26.1 "	51.9 "	0.7 "
$\text{LiClO}_4/\text{CuCl}_2$	17.7 "	25.7 "	51.0 "	0.7 "
$\text{LiClO}_4/\text{CuF}_2$	17.6 "	25.0 "	45.5 "	0.5 "
$\text{LiAlCl}_4/\text{CuCl}$	19.3 "	33.6 "	50.6 "	13.8 "
$\text{LiAlCl}_4/\text{CuCl}_2$	20.8 "	29.7 "	41.1 "	15.3 "
$\text{LiAlCl}_4/\text{CuF}_2$	17.8 "	24.0 "	44.0 "	11.7 "

Table 2 (Con't)
Conductivities of Copper-salt-lithium salt Solutions

Salt Combination	Conductivity			
	(ohm ⁻¹ cm ⁻¹)			
	propylene carbonate	butyro- lactone	dimethyl- formamide	tetrahydro- furan
LiBF ₄ /CuCl	16.7 x 10 ⁻⁴	24.9 x 10 ⁻⁴	54.6 x 10 ⁻⁴	0.4 x 10 ⁻⁴
LiBF ₄ /CuCl ₂	16.7 "	24.4 "	41.1 "	0.3 "
LiBF ₄ /CuF ₂	16.5 "	22.6 "	48.5 "	0.2 "

Further examination of the tetrahydrofuran solutions was not undertaken because of the low conductivities.

(2) Spectrophotometric Analysis for copper (II).

It was found that the concentration of copper (II) could be conveniently determined in each case by simply diluting a ten-ml. aliquot of the solution to 100 ml. with an aqueous solution, 1 M in NH₃ and 1 M in NH₄Cl. The concentration of the blue ammonia-copper complex was determined by measuring the optical absorbance at 6200 Å and comparing the results with a series of standard solutions. This analysis was not performed on the dimethylformamide solutions since the electrochemical investigations later described indicated that the solubility of copper salts in all cases was greater in dimethylformamide than in butyrolactone or propylene carbonate. In table 3 are shown the results obtained. The copper salt was, in fact, completely soluble in those solutions with values greater than 0.046 M l⁻¹, and the deviation from the value of 0.05 M l⁻¹, the amount of copper actually added, is merely experimental error.

Table 3
Solubility of copper (II) in copper salt-lithium salt solutions

Salt combination	Solvent	
	Concentration of copper (II)	
	(M l ⁻¹)	
	propylene carbonate	butyrolactone
LiCl/CuCl ₂	0.049	0.049
LiCl/CuF ₂	0.029	0.030
LiClO ₄ /CuCl ₂	0.048	0.008
LiClO ₄ /CuF ₂	0.027	0.002
LiAlCl ₄ /CuCl ₂	0.023	0.046
LiAlCl ₄ /CuF ₂	0.013	0.010
LiBF ₄ /CuCl ₂	0.049	0.006
LiBF ₄ /CuF ₂	0.022	none

d. Discussion. A comparison of the conductivity data shown in table II-1 with the copper concentration shown in table II-2 is interesting in disclosing that there is not an increase in conductivity proportionate with increasing solubility of copper species. This indicates that copper does not dissolve ionically or combine with the electrolyte to furnish a solution of different ionic composition.

The greater solubility of copper in propylene carbonate solutions of LiClO₄ and LiBF₄ versus that in butyrolactone solutions of the same salts was noted, as was the greater solubility observed in chloride media.

2. Solubilization of copper salts in chloride media.

a. Experimental. The dissolution of copper salts through complexation with chloride ions was studied by means of conductimetric

titrations. In these experiments solid copper salts were added to samples of the solvent indicated in such an amount that, if totally soluble, the concentration would be 0.1 M l^{-1} . To each solution were added portions of solid LiCl and the conductivity measured after equilibration was indicated by the constancy of such measurements over a period of time. Equilibration was very slow in the CuF_2 systems and each datum shown in table 5 is for a separate solution which had been allowed to equilibrate for over a week.

b. Results. In table 4 below are shown the results obtained when CuCl_2 in propylene carbonate was titrated with LiCl. The concentration of LiCl given is not that actually present in solution but the amount which would be present if totally soluble.

Table 4
Conductimetric Titration of CuCl_2 with LiCl

Concentration of LiCl added if totally soluble (M l^{-1})	Specific Conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$)
0.00	1.2×10^{-4}
0.049	10.0×10^{-4}
0.103	18.7×10^{-4}
0.154	23.4×10^{-4}
0.21	24.8×10^{-4}
0.27	24.8×10^{-4}
0.33	22.4×10^{-4}

These results indicate that copper largely dissolves by the reaction:
 $\text{LiCl} + \text{CuCl}_2 = \text{Li}^+ + \text{CuCl}_3^-$.

An identical titration was performed using CuCl rather than CuCl_2 . When LiCl had been added in sufficient quantity to make the solution 0.1 M if totally soluble the specific conductance was $21.4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$; tripling the amount of LiCl increased the conductance negligibly to $22.9 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. These results indicate that copper largely dissolves by the reaction: $\text{CuCl} + \text{LiCl} = \text{Li}^+ + \text{CuCl}_2^-$.

In Table 5 below are shown the results obtained when LiCl was added to CuF_2 in butyrolactone.

Table 5
Conductimetric Titration of CuF_2 with LiCl

Concentration of LiCl added, if totally soluble	Analytically determined concentration of Cu	Specific Conductance
(M l^{-1})	(M l^{-1})	($\text{ohm}^{-1} \text{ cm}^{-1}$)
0.03	0.0125	1.57×10^{-4}
0.06	0.0145	3.04×10^{-4}
0.10	0.0261	7.65×10^{-4}
0.13	0.0343	10.9×10^{-4}
0.16	0.0400	12.3×10^{-4}
0.25	0.0452	13.53×10^{-4}
0.35	0.691	17.0×10^{-4}
0.45	0.795	19.4×10^{-4}

The results indicate the solubilization of CuF_2 through chloride complexation but are not sufficiently clear-cut to indicate the stoichiometry of the solubilizing reaction.

c. Conclusions. The solubilization of copper through complexation with chloride ions is demonstrated.

3. Solubilization of copper salts by impurities.

It was feared that the rather larger solubility of copper salts in propylene carbonate versus butyrolactone as shown in Table II-2 might be due to impurities in the propylene carbonate. This was indeed found to be true as discussed below.

a. Experimental. A sample of the same propylene carbonate which had been used in the preliminary screening experiments and in which the solubility data shown in Table II-2 were obtained, was further investigated by making the solution 0.1 M in LiClO_4 . A plot of E vs. $it^{1/2}$ was prepared and was similar to that shown in Figure 10 for fraction 2. A freshly distilled batch of propylene carbonate was examined in the same fashion and the resultant E vs. $it^{1/2}$ curves had an appearance essentially identical with that shown in Figure 10 for fraction 5. This solution was then saturated with excess CuCl_2 and allowed to stand with stirring overnight. The concentration of copper (II) in the solution was determined spectrophotometrically. The solution was found to be 0.0123 M in Copper (II). The previous results shown in table II-2 indicated copper to be completely soluble in this solution.

b. Discussion. A clear correlation between solution impurity as determined from the behavior of the lithium electrode and solubility of CuCl_2 indicates that impurities may have serious effects in solubilizing cathode salts. Such results cast doubt on solubility data without some independent assessment of impurity levels.

C. Electrochemical Behavior of Solutions of Copper Salts.

1. Preliminary Screening Experiments -- Polarographic Examination

a. Experimental. The various solutions prepared for the initial screening experiments described above were subjected to polarographic examination. The polarographic apparatus consists of a conventional dropping mercury electrode the capillary of which is surrounded by a

silver wire helix which serves as the counter electrode. A conventional H-cell is used and a silver helix in the side compartment serves as the reference electrode. As in all of our previous work, no claim whatsoever is made regarding the thermodynamic significance of the potential of such a reference electrode. During the past eighteen months it has been consistently observed that a silver metal electrode placed in propylene carbonate or butyrolactone solutions assumes a well-poised, satisfactorily reproducible potential. The potential of a lithium-lithium ion electrode versus the silver electrode is consistently observed to be about -3.0 V. The potential of a silver-silver ion electrode versus the silver electrode in the absence of silver ions is consistently observed to be about $+0.8$ V.

The instrumentation used has been especially constructed for use in poorly conducting solutions. In the conventional apparatus the X-axis gives the applied voltage across the entire cell. The Y-axis gives the current. In our apparatus a fast response X-Y recorder is used, the X-axis measures, not the applied voltage, but the potential between the working and reference electrodes. The Y-axis measures the current from the voltage drop across precision resistors in series with the cell. The instrumentation is such that the maximum current rather than the average damped current is measured.

b. Results. A typical polarogram is shown in Figure 14.

This polarogram was obtained in propylene carbonate, 0.1 M in LiAlCl_4 and to which CuF_2 had been added and found, spectrophotometrically, to dissolve to the extent of 0.013 M l^{-1} .

c. Discussion.

(1) Region I: 0 to -1.0 V. A rather ill-defined diffusion current plateau, the first diffusion current plateau, is often observed but is as often obscured by the large maximum, the first maximum, which appears

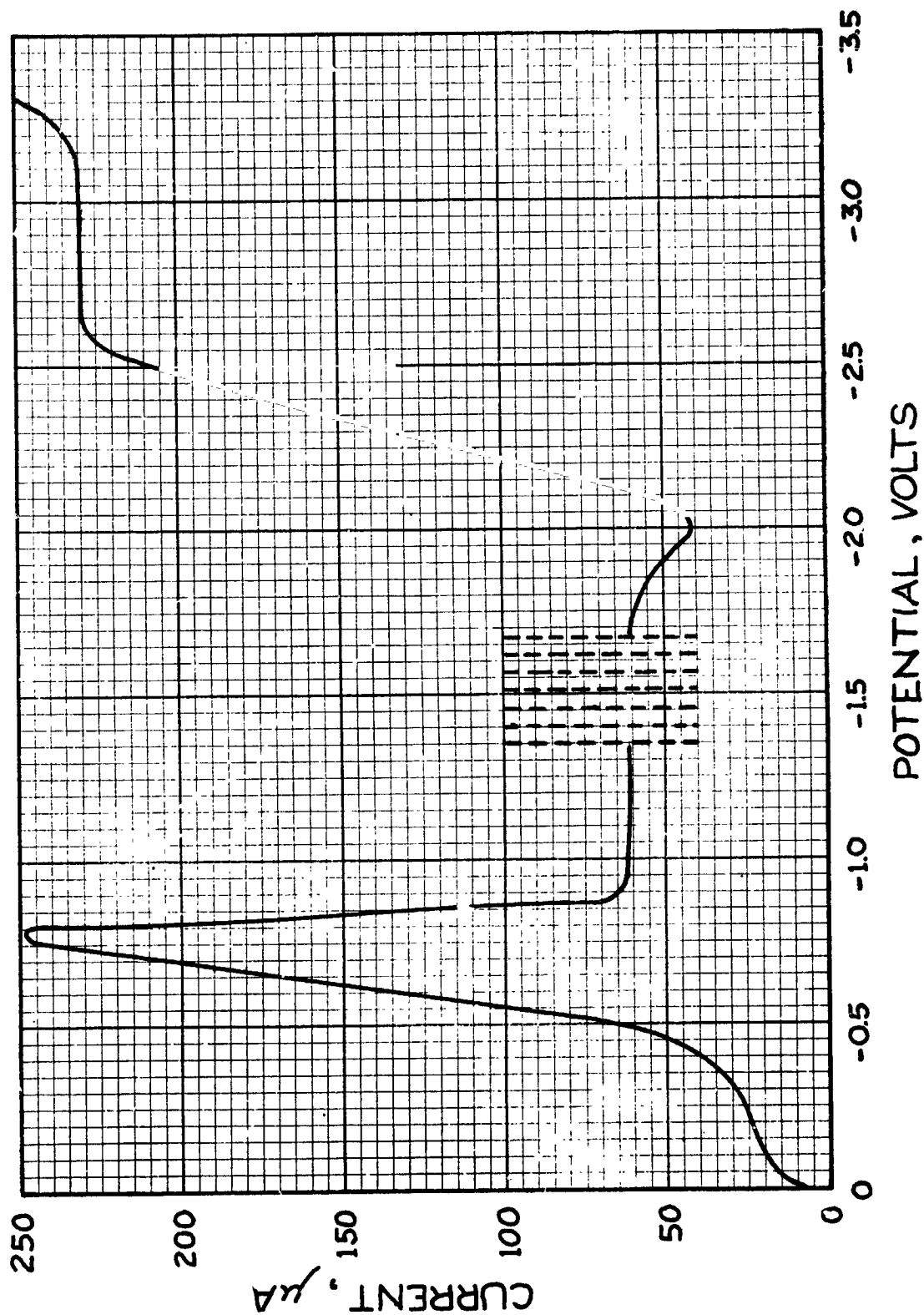


Figure 14: Polarography in copper (II)/chloride Media.

This polarogram, obtained on a dropping mercury electrode in propylene carbonate, 0.1 M in LiAlCl_4 and 0.013 M in CuF_2 , has been selected for the purpose of discussion as most conveniently illustrating the variety of phenomena encountered in the various solutions.

between -0.5 and -1.0 V. This maximum is observed in nearly all solutions and there is no correlation between its shape, height, breadth, and composition of the solution.

When a reasonably well defined first diffusion current plateau is observed its height is related to the concentration of copper in the solution; however, the proportionality constant varies between $1200 \mu\text{A/C}(\text{M l}^{-1})$ and $3500 \mu\text{A/C}(\text{M l}^{-1})$ which is of the same order of magnitude as that for lithium ($2600 \mu\text{A/C}(\text{M l}^{-1})$). The variation in proportionality constant precludes stating whether the reduction along the first diffusion current plateau is a one or two electron reduction.

(2) Region II: -1.0 to -2.0V. If the first maximum is not too broad a second diffusion current plateau is observed at between -1.0 and -1.2 V. At about -1.5 V a variety of ill-defined and erratic phenomena occur. The recorder may undergo erratic excursions or a well defined second maximum may be observed. These effects are simply denoted by the verticle dotted lines. The second maximum is followed by a continuation of the second diffusion current plateau, though the height may be diminished by as much as 20%. In the eight cases where reasonably well-defined first and second diffusion current plateaus were observed it was found that the height of the second is twice that of the first in chloride media and equal to that of the first in solutions in which chloride is totally absent.

The second maximum is especially prominent in solutions of LiAlCl_4 and is completely absent in all solutions of LiClO_4 and LiBF_4 .

(3) Region III: -2.0 to 3.5 V. At between -2.0 and -2.5 V a linear increase in current with potential occur. This is observed in solutions of LiClO_4 and LiBF_4 alone, in which the height of the subsequent third diffusion current plateau is proportional to the concentration of lithium salt. As noted above the proportionality constant is $2600 (\mu\text{A/C}(\text{M l}^{-1}))$.

The third diffusion current plateau extends from 0.2 to 0.5 V following which an increase in current signals the onset of a further reduction process.

d. Conclusions. The basic utility of polarographic investigations in determining the solubility of copper salts is suggested. However, the results obtained thus far have not been for solutions in which a true excess of supporting electrolyte existed. The diffusion current plateaus will reflect the movement of ions by both diffusion and electrical migration to varying degrees depending on the nature and relative amounts of the solutes. In the absence of supporting electrolyte the proportionality between concentration and diffusion current plateau height may easily vary by a factor of two as was indeed observed. In future work the polarographic determination of solubility will be made in excess supporting electrolyte.

2. Preliminary Screening Experiments --Solid Electrode Behavior.

The reduction behavior of the various propylene carbonate, butyrolactone, and dimethylformamide solutions was examined by obtaining plots of $iT^{1/2}$ vs. E. for each solution. The data were not satisfactory since a true excess of supporting electrolyte was not present, thus a clear correlation between the concentration of dissolved copper and the observed values for $iT^{1/2}$ could not be made. It was evident that the reduction of copper species was complex and a more detailed examination of this reduction was undertaken as described in the next section.

3. Electrochemical Behavior in Solutions of Copper and Chloride.

a. Experimental. Various solutions were examined. The most detailed experiments were performed in the following solutions:

(1) Propylene carbonate, 0.1 M in LiClO_4 , to which was added enough solid CuCl_2 to make the solution 0.025 M if totally soluble, and enough solid LiCl to make the solution 0.05 M if totally soluble.

(2) Propylene carbonate, 0.1 M in LiBF_4 , saturated with CuCl_2 . The concentration of total copper determined spectrophotometrically was 0.013 M.

(3) Propylene carbonate, 0.1 M in LiBF_4 , to which was added enough solid CuCl_2 to make the concentration of copper 0.02 M if totally soluble. The solution was then saturated in LiCl .

(4) Propylene carbonate, 0.1 M in CuCl_2 saturated with LiCl .

These solutions were examined in a variety of ways as discussed below.

b. Results. The entire range of electrochemical techniques discussed in section 1 of this report were applied. The results are very simply summarized. The reduction and oxidation of copper species proceeds in one-electron steps. In Table 6 are shown the measured potentials for the four processes with respect to a lithium electrode in the same solution.

Table 6
Copper Redox Couples in Chloride Media

Reaction	Measured Potential vs. Li^0/Li^+ Electrode (V)	Equilibrium Reduction Potential vs. Li^0/Li^+ Electrode (V)
$\text{Cu}^{++} + e^- = \text{Cu}^+$	+3.2 to +2.7	+3.3*
$\text{Cu}^+ = \text{Cu}^{++} + e^-$	+3.5 to +3.7	+3.3*
$\text{Cu}^+ + e^- = \text{Cu}^0$	+2.1 to +1.6	+2.6**
$\text{Cu}^0 = \text{Cu}^+ + e^-$	+3.1	+2.6**

* Average of four potentials given in middle column.

** Average of potentials observed during cathodic deposition of copper from copper (I) solution at 0.75 mA cm^{-2} followed by current reversal and anodic dissolution.

Using a potential of +3.3 V as the reduction potential for the copper (II)/copper (I) couple and +2.6 V as the reduction potential for the copper (I)/copper (0) couple one calculates an equilibrium constant for the reaction $\text{Cu}^{++} + \text{Cu}^0 = 2 \text{Cu}^+$ of about 1.6×10^{11} , which indicates the reaction should go essentially to completion. This is observed, as described later in this section.

In figure 15 curve a is a plot of $it^{1/2}$ vs. E obtained in a propylene carbonate solution, 0.1 M in CuCl_2 , which had been saturated with LiCl. The chronopotentiograms from which this data is obtained were done on polished platinum electrodes. The potential in figure II-2 is with reference to a silver disc in the same solution. The potential of a lithium electrode in this solution is -3.2 V versus the reference silver disc electrode. It will be observed that reduction commences at about +0.2 V vs. the reference silver disc (i.e. about +3.4 V vs. the lithium electrode). An $it^{1/2}$ plateau is observed between 0 and -1 V. The solution was deep reddish-orange, the color of the copper-chloride complex. Prolonged cathodic reduction was performed at potentials between 0 and -0.5 V. Upon overnight electrolysis at such potentials the color of the solution disappeared. No copper deposited on the platinum electrodes. This is considered sufficient evidence that a one electron reduction of copper (II) to copper (I) occurs, resulting in a solution of the colorless copper (I) chloride complex. Solutions of copper (I) are also conveniently prepared by simply placing a copper coil in the solution and stirring overnight, whereupon the copper (II) reacts with copper metal to produce copper (I) as described above.

Solutions of copper (I) display no cathodic reduction potentials more positive than about -0.6 V (+2.6 V vs. the lithium electrode). Curve b of figure II-2 shows the $it^{1/2}$ vs. E curve obtained in a solution, initially 0.1 M in CuCl_2 , which had been saturated with LiCl and then allowed to stand overnight in contact with a copper coil. It will be observed that the

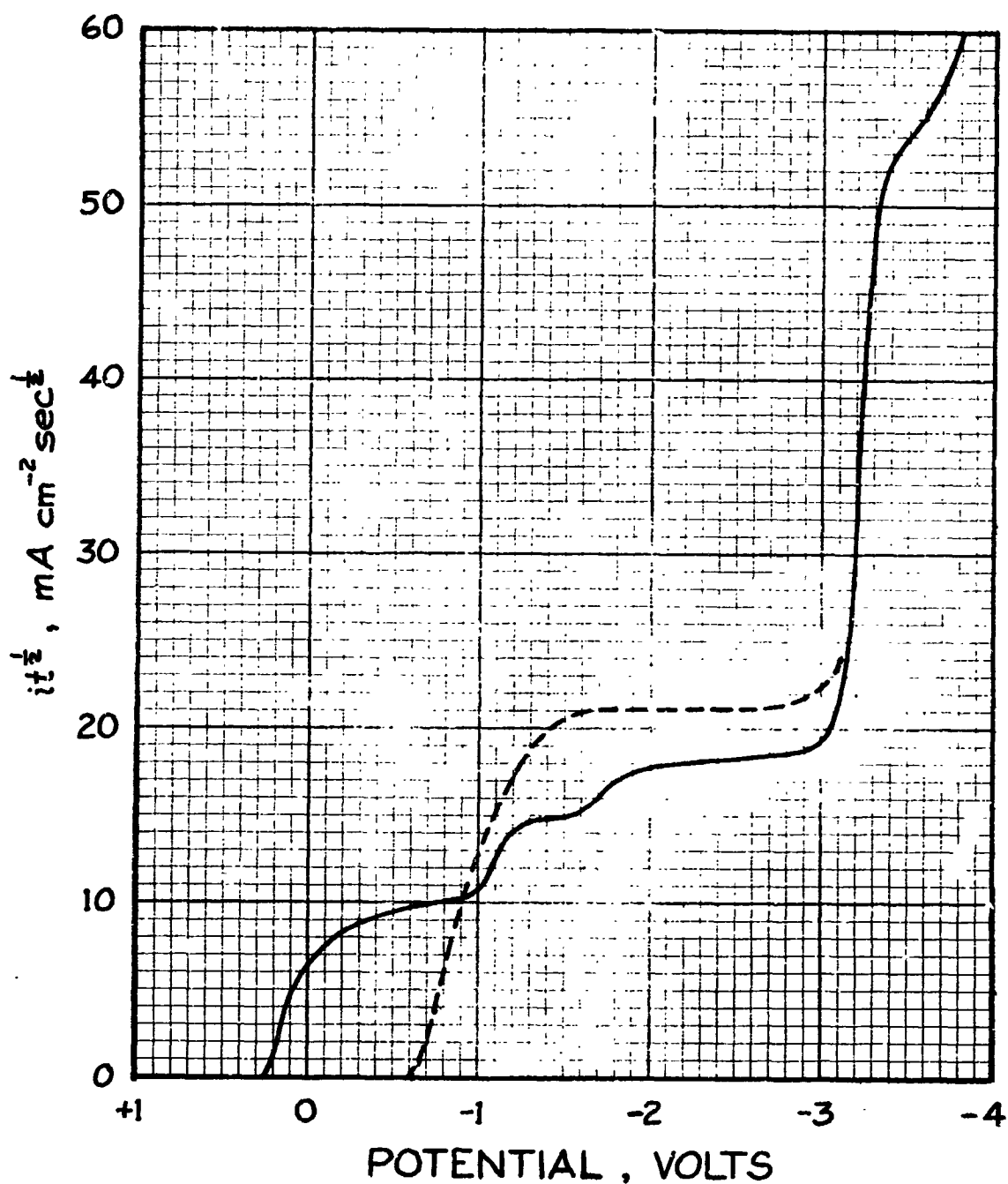


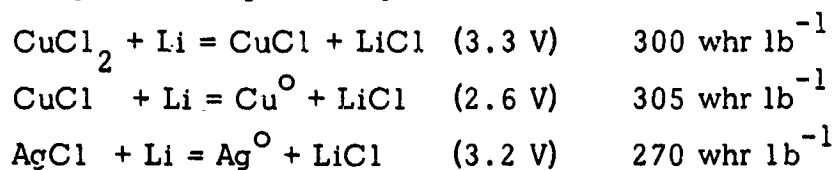
Figure 15: E vs. $it^{1/2}$ curves in copper (I) and copper (II) - chloride media

Potentials are given with respect to the silver/silver chloride reference electrode in the same solution and have been corrected for iR drop. See discussion for further details.

$iT^{1/2}$ plateau is about double that in the original copper (II) solution. This is because the concentration of copper (I) produced by the reaction between copper (II) and the metal is double the initial concentration of copper (II). When subjected to prolonged electrolysis at -1.5 V vs. the silver electrode, copper metal is deposited with about 80-90% current efficiency. Anodic chronopotentiograms can also be obtained in solutions of copper (I) for the reaction: $Cu^+ = Cu^{++} + e^-$, and the anodic $iT^{1/2}$ is the same as that observed on cathodic reduction.

The reduction behavior observed between -1 and -3 V in copper (II) solutions is quite peculiar. Steady state currents could not be obtained in this potential range; in fact, the current rapidly decayed to negligible values. Metallic copper could not be deposited from solutions of copper (II). One would expect that, since no problem obtains in getting copper deposition from solutions of copper (I), one should with equal ease be able to obtain the two-step reduction of copper (II) to the metal, via the copper (I) species. We have no explanation for this unusual behavior. The general statement may be made that the copper (I) species produced at the electrode surface by the reduction of copper (II) is not the same as the species normally present in solutions of copper (I) and is not itself capable of further reduction, perhaps because of the formation at the electrode surface of passivating films of $LiCl$.

d. Discussion. The utility of a copper system operating in chloride media appears doubtful because of the solubilization of copper salts and the two step nature of the electrode reactions. This is indicated by the energy densities calculated for the reactions shown below, using the potentials given in parentheses.



4. Electrochemical Behavior of CuF_2 electrodes.

There yet exists no electrolyte in which copper metal may be anodically oxidized to an insoluble fluoride salt. Experiments with copper fluoride electrodes therefore involve the fabrication of electrodes incorporating the salt.

a. Experiment 1. Pellet electrodes of CuF_2 were prepared by compressing a powder, 20% by weight of CuF_2 and 80% by weight of copper powder. These pellets (ca. 0.8 cm^2 in area) were incorporated in a standard Mallory RM-635 cell container together with a disc of lithium metal separated from the CuF_2 electrode by a fiber glass separator impregnated with a saturated solution of LiBF_4 in butyrolactone.

The polarization characteristics of the cell are shown in figure 16. This curve was obtained by applying constant current of the magnitude indicated for 2 minutes. The linearity of the curve suggests that the iR drop across the separator dominates the polarization characteristics.

The electrokinetic reversibility of the electrochemical system is evidenced by the fact that repeated excursion between high and low currents continued to give measurements lying along the curve shown in figure 16.

No attempts were made to determine the utilization efficiency of the cells or the self-discharge characteristics of the cells but only to establish that the electrokinetic reversibility of the CuF_2 electrode appears satisfactory.

b. Experiment 2. Cu-LiF electrodes were prepared by sintering together equal parts by weight of copper powder and lithium fluoride in argon atmospheres at $650\text{--}700^\circ \text{C}$ for one-half hour. Subsequent electrochemical measurements were performed in excess electrolyte under

conditions essentially identical to those employed with the lollipop disc electrodes.

The electrodes were anodized at constant current and after varying periods of time the current was reversed and the cathodic utilization determined. Similar experiments were employed using sintered copper electrodes without the incorporation of LiF. Both sets of experiments were performed in propylene carbonate solutions, 1.0 M in LiBF_4 . Low and equal cathodic utilization was obtained in both cases indicating that the fluoride contained in LiF is not available for formation of CuF or CuF_2 .

c. Experiment 3. Cu-LiF and Cu-LiCl electrodes were prepared by sintering equal parts by weight of copper and lithium chloride or fluoride under the same conditions as described in experiment 2 above.

The electrodes were cathodized in a large excess of propylene carbonate, 1.0 M in $\text{Mg}(\text{ClO}_4)_2$. On cathodization of the Cu-LiF electrode at 1 mA cm^{-2} the potential immediately rose to -10 V (versus a silver disc in the same solution). On cessation of cathodization the potential rapidly decayed to -1.0 V versus a silver disc. There was no indication of lithium deposition and immersion of the electrode in aqueous solution produced no effect. Cathodization of the Cu-LiCl electrode under the same conditions did result in the deposition of lithium metal. The potential during cathodization remained slightly negative to -3.0 V versus a silver disc. On cessation of cathodization the open circuit voltage remained constant at about -3.0 V, and vigorous gassing ensued when the electrode was plunged into water.

These results suggest that the failure to obtain insoluble fluoride films on copper on anodization via the insoluble LiF imbedded in the copper matrix may be a kinetic effect resulting from the large lattice energy of LiF.

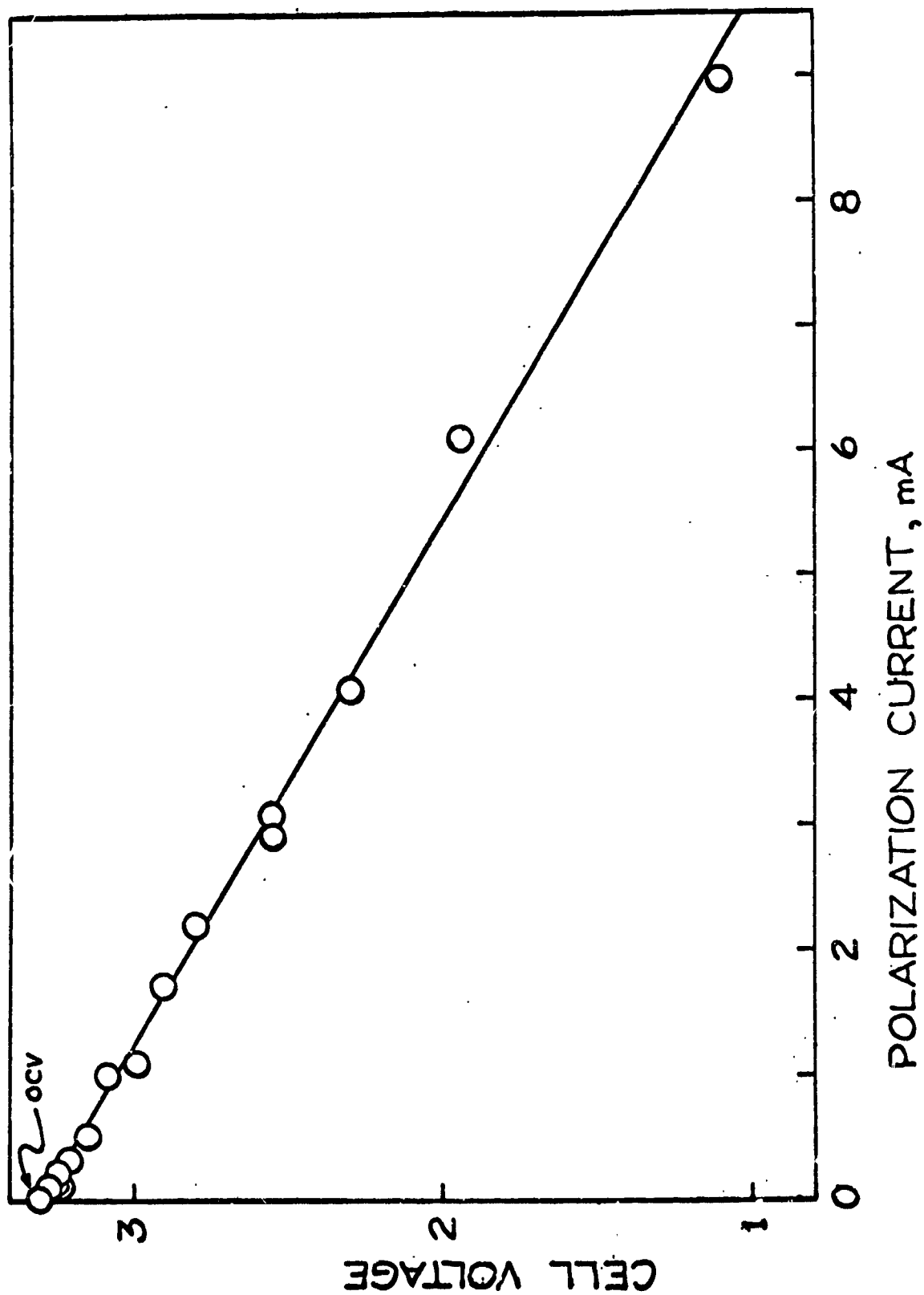


Figure 16: Polarization Behavior of CuF_2/Li Cell

See discussion for details.

III. ELECTROCHEMICAL BEHAVIOR OF SILVER, COBALT, NICKEL, IRON AND SOLVENT

A. Cycling behavior of silver, cobalt, nickel, and iron.

1. Experimental. In these experiments metal discs contained in the lollipop configuration are subjected to anodization at various currents for 10 sec. followed by current reversal. Of interest is the potential at which anodization and subsequent cathodization occurs, and the cathodic utilization of anodically formed products. Typical results are shown in Figure 17. The behavior there displayed is consistently observed in propylene carbonate and butyrolactone solutions of LiAlCl_4 and LiBF_4 with but one variation, the silver salt formed on anodization in LiAlCl_4 solutions is insoluble. Most striking is the marked irreversibility of the cobalt, iron, and nickel electrodes as indicated by the large difference between anodic and cathodic potentials.

In Table 7 below are shown typical results. These results were obtained in butyrolactone solutions, 0.1 M in LiBF_4 , and show the best reversibility thus far found. The potential before the slash is that observed on anodization; The potential after the slash is that observed on subsequent cathodization. Potentials are with respect to the silver disc reference electrode.

Table 7
Cycling Behavior of Silver, Copper, Iron, Cobalt and Nickel

Metal	Cycling Current (mA cm ⁻²)					
	1	1.8	3.2	5.6	10	20
Silver	+.46/+.42	+.49/+.46	+.49/+.45	+.53/+.42	+.48/+.40	+.38/+.24
Copper	+.42/+.30	+.41/+.28	+.44/+.28	+.44/+.28	+.44/+.27	+.37/+.25
Iron	+.50/-.75	+.53/-1.3	+.55/-1.3	+.55/-1.2	+.60/-1.15	+.6/-1.15
Nickel	+1.8/-1.2	+2.0/-1.1	+2.2/-0.9	+2.2/-0.9	+3.8/-.7	+.4.0/-.7
Cobalt	+.75/-1.8	+.75/-1.9	+.75/-1.8	+.85/-1.8	+.85/-1.6	+.8/-1.1

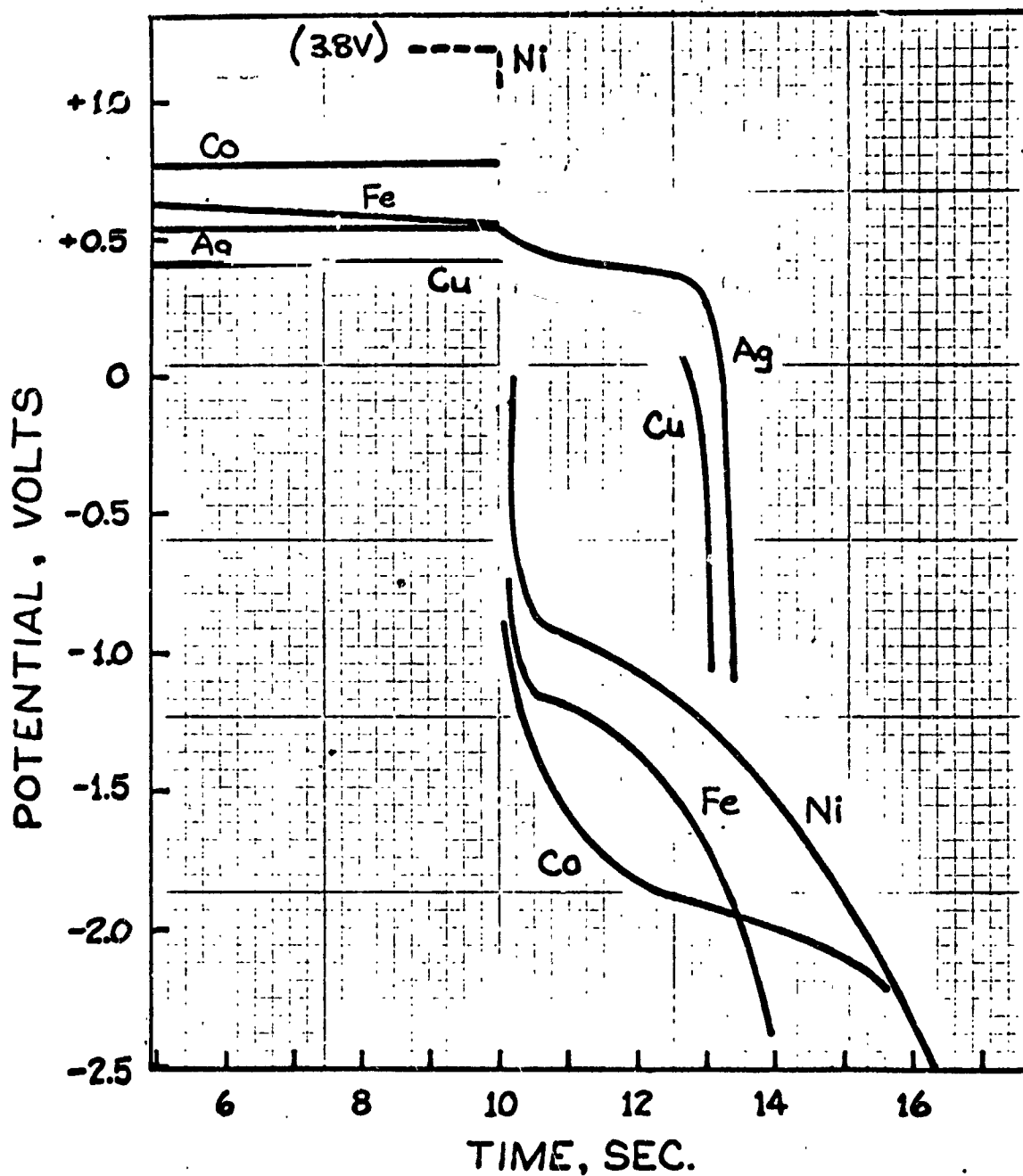


Figure 17: Examples of Cycling Behavior

Results obtained in butyrolactone, 0.1 M in LiBF_4 , at 5.6 mA cm^{-2} . Potentials are corrected for iR drop and given with respect to the reference silver disc electrode in the same solution. The open circuit potential of the lithium electrode is about -3.0 V versus the silver disc electrode.

2. Discussion. No evidence has yet been found that redox couples involving metallic iron, cobalt, or nickel can be satisfactory cycled in propylene carbonate, butyrolactone, or dimethylformamide.

B. Anodic Decomposition of Solvent.

The term, decomposition potential, is a rather meaningless term for irreversible electrode processes, since the potential at which electrolytic decomposition occurs is a function of the current. The anodic decomposition of propylene carbonate, 0.1 M in LiClO_4 , was studied on polished platinum electrodes. These experiments were performed by anodizing the electrode potentiostatically in stirred solutions; satisfactory steady state currents were rapidly obtained. A satisfactorily linear Tafel plot was obtained at currents from 0.005 to 23 mA cm^{-2} , given by the equation:

$$E = +2.5 \text{ (vs. silver disc R.E.)} + 0.34 \log i \text{ (mA cm}^{-2}\text{)}$$

The Tafel slope of 0.34 V is quite large, suggesting a transfer coefficient of only 0.17 for a one-electron oxidation. Obviously the electrolyte is quite stable to anodic decomposition on platinum.

It was interesting to observe that the anodic decomposition products could be reduced on current reversal. Electrodes were subjected to prolonged anodization in quiet solution at 4 mA cm^{-2} , the potential was about +2.7 V vs. the reference silver disc. On current reversal cathodic reduction was observed at about -0.5 V vs. the reference silver disc, with about 30% utilization.